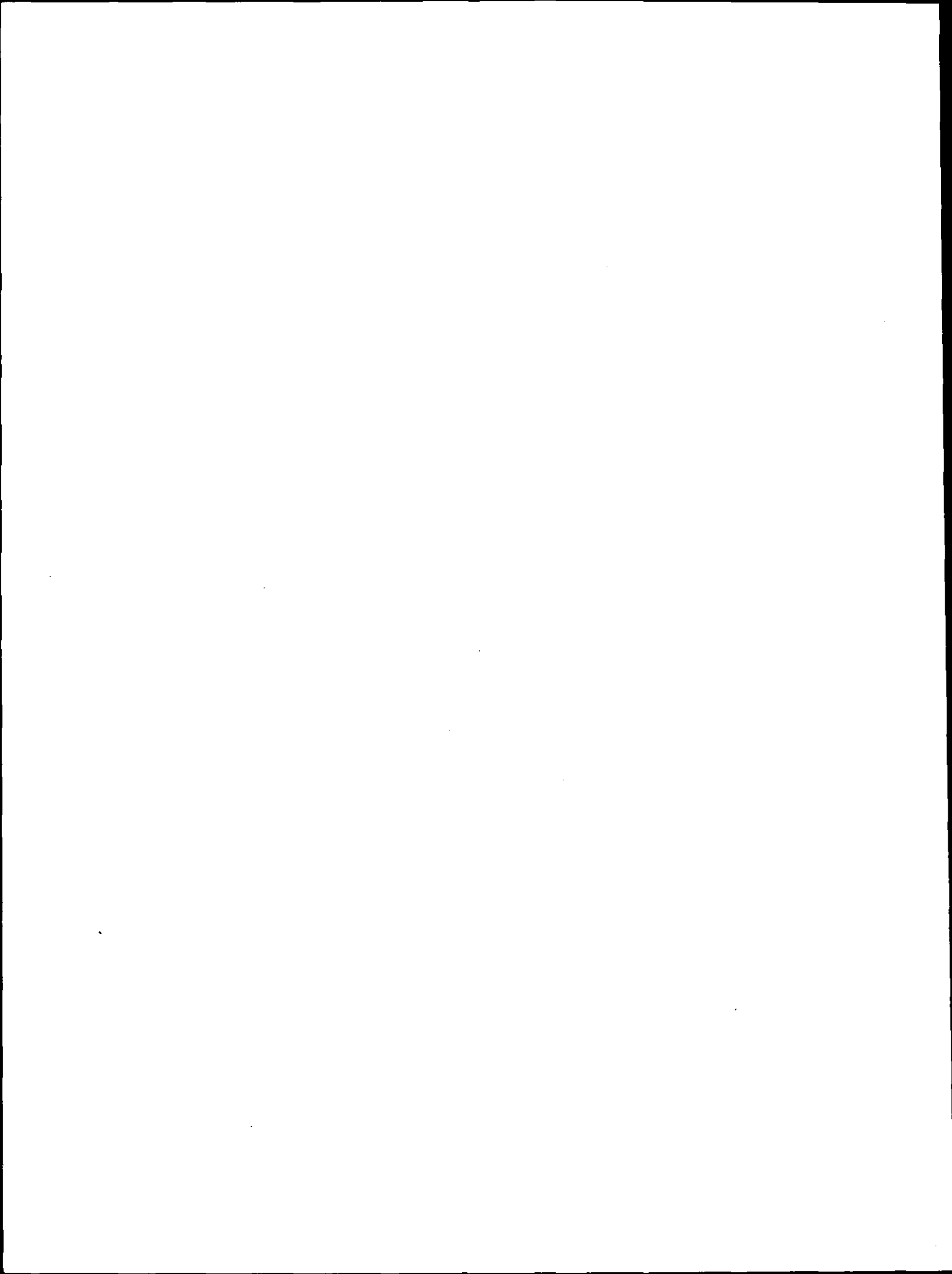


Air Quality Criteria for Particulate Matter

Volume I

Fourth External Review Draft



Air Quality Criteria for Particulate Matter

Volume I

National Center for Environmental Assessment-RTP Office
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC



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PREFACE

National Ambient Air Quality Standards (NAAQS) are promulgated by the United States Environmental Protection Agency (EPA) to meet requirements set forth in Sections 108 and 109 of the U.S. Clean Air Act (CAA). Sections 108 and 109 require the EPA Administrator (1) to list widespread air pollutants that reasonably may be expected to endanger public health or welfare; (2) to issue air quality criteria for them that assess the latest available scientific information on nature and effects of ambient exposure to them; (3) to set "primary" NAAQS to protect human health with adequate margin of safety and to set "secondary" NAAQS to protect against welfare effects (e.g., effects on vegetation, ecosystems, visibility, climate, manmade materials, etc.); and (5) to periodically (every 5 years) review and revise, as appropriate, the criteria and NAAQS for a given listed pollutant or class of pollutants.

The original NAAQS for particulate matter (PM), issued in 1971 as "total suspended particulate" (TSP) standards, were revised in 1987 to focus on protecting against human health effects associated with exposure to ambient PM less than 10 microns ($\leq 10 \mu\text{m}$) that are capable of being deposited in thoracic (tracheobronchial and alveolar) portions of the lower respiratory tract. Later periodic reevaluation of newly available scientific information, as presented in the last previous version of this "Air Quality Criteria for Particulate Matter" document published in 1996, provided key scientific bases for PM NAAQS decisions published in July 1997. More specifically, the PM_{10} NAAQS set in 1987 ($150 \mu\text{g}/\text{m}^3$, 24-h; $50 \mu\text{g}/\text{m}^3$, annual average) were retained in modified form and new standards ($65 \mu\text{g}/\text{m}^3$, 24-h; $15 \mu\text{g}/\text{m}^3$, annual average) for particles $\leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) were promulgated in July 1997.

This Fourth External Review Draft of revised Air Quality Criteria for Particulate Matter assesses new scientific information that has become available mainly between early 1996

1 through April 2002. The present draft is being released for public comment and review by the
2 Clean Air Scientific Advisory Committee (CASAC) to obtain comments on the organization and
3 structure of the document, the issues addressed, the approaches employed in assessing and
4 interpreting the newly available information on PM exposures and effects, and the key findings
5 and conclusions arrived at as a consequence of this assessment. Public comments and CASAC
6 review recommendations will be taken into account in making any appropriate further revisions
7 to this document for incorporation into a final draft. Evaluations contained in the present
8 document will be drawn on to provide inputs to associated PM Staff Paper analyses prepared by
9 EPA's Office of Air Quality Planning and Standards (OAQPS) to pose alternatives for
10 consideration by the EPA Administrator with regard to proposal and, ultimately, promulgation of
11 decisions on potential retention or revision of the current PM NAAQS.

12 Preparation of this document was coordinated by staff of EPA's National Center for
13 Environmental Assessment in Research Triangle Park (NCEA-RTP). NCEA-RTP scientific
14 staff, together with experts from other EPA/ORD laboratories and academia, contributed to
15 writing of document chapters; and earlier drafts of this document were reviewed by experts from
16 federal and state government agencies, academia, industry, and non-governmental organizations
17 (NGOs) for use by EPA in support of decision making on potential public health and
18 environmental risks of ambient PM. The document describes the nature, sources, distribution,
19 measurement, and concentrations of PM in outdoor (ambient) and indoor environments. It also
20 evaluates the latest data on human exposures to ambient PM and consequent health effects in
21 exposed human populations (to support decision making regarding primary, health-related PM
22 NAAQS). The document also evaluates ambient PM environmental effects on vegetation and
23 ecosystems, visibility, and man-made materials, as well as atmospheric PM effects on climate
24 change processes associated with alterations in atmospheric transmission of solar radiation or its
25 reflectance from the Earth's surface or atmosphere (to support decision making on secondary
26 PM NAAQS).

27 The NCEA of EPA acknowledges the contributions provided by authors, contributors, and
28 reviewers and the diligence of its staff and contractors in the preparation of this document.
29

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Abbreviations and Acronyms

AAS	atomic absorption spectrophotometry
AC	air conditioning
ACGIH	American Conference of Governmental Industrial Hygienists
ACS	American Cancer Society
ADS	annular denuder system
AES	atomic emission spectroscopy
AIRS	Aerometric Information Retrieval System
ANC	acid neutralizing capacity
AQCD	Air Quality Criteria Document
AQI	Air Quality Index
ARIES	Aerosol Research and Inhalation Epidemiology Study
ASOS	Automated Surface Observing System
ATOFMS	time-of-flight mass spectrometer
AWOS	Automated Weather Observing System
BaP	benzo(a)pyrene
BASE	Building Assessment and Survey Evaluation
BC	black carbon
BNF	bacterial nitrogen fertilization
BOSS	Brigham Young University Organic Sampling System
BYU	Brigham Young University
CAA	Clean Air Act
CAAM	continuous ambient mass monitor
CAMNET	Coordinated Air Monitoring Network
CARB	California Air Resources Board
CASAC	Clean Air Scientific Advisory Committee
CASTNet	Clean Air Status and Trends Network

C _B	base cations
CC	carbonate carbon
CCPM	continuous coarse particle monitor
CCSEM	computer-controlled scanning electron microscopy
CEN	European Standardization Committee
CFCs	chlorofluorocarbons
CFR	Code of Federal Regulations
CHAD	Consolidated Human Activity Database
CIF	charcoal-impregnated cellulose fiber
CIIT	Chemical Industry Institute of Technology
CMAQ	Community Multi-Scale Air Quality
CMB	chemical mass balance
CMSA	Consolidated Metropolitan Statistical Area
CO CD	Air Quality Criteria Document for Carbon Monoxide
COD	coefficient of divergence
COPD	chronic obstructive pulmonary disease
CPC	condensation particle counter
CRP	Coordinated Research Program
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CSMCS	Carbonaceous Species Methods Comparison Study
CSS	coastal sage scrub
CTM	chemistry-transport model
CV	coefficient of variation
CVM	contingent valuation method
D _a	aerodynamic diameter
DAQ	Department of Air Quality
DCFH	dichlorofluorescein
DMPS	differential mobility particle sizer

DMS	dimethyl sulfide
D _p	particle diameter
dv	deciview index
EAD	electrical aerosol detector
EC	elemental carbon
ECAO	Environmental Criteria and Assessment Office
EDXRF	energy dispersive X-ray fluorescence
EEA	Essential Ecological Attributes
ENSO	El Nino-Southern Oscillation
EPA	Environmental Protection Agency
ESP	electrostatic precipitator
ETS	environmental tobacco smoke
EXPOLIS	Air Pollution Exposure Distribution within Adult Urban Populations in Europe
FID	flame ionization detection
FRM	Federal Reference Method
GAM	general additive models
GC	gas chromatography
GCMs	General Circulation Models
GCVTC	Grand Canyon Visibility Transport Commission
GC/MSD	gas chromatography/mass-selective detection
GHG	greenhouse gases
GSD	geometric standard deviation
HBEF	Hubbard Brook Experiment Forest
HDS	honeycomb denuder/filter pack sampler
HEADS	Harvard-EPA Annular Denuder Sampler
HEI	Health Effects Institute
HI	Harvard Impactors
hivol	High volume sampler

HTGC-MS	high temperature gas chromatography-mass spectrometry
HVAC	heating, ventilation, or air conditioning
IC	ion chromatography
ICP	inductively coupled plasma
IFS	Integrated Forest Study
IMPROVE	Interagency Monitoring of Protected Visual Environments
INAA	instrumental neutron activation analysis
IOVPS	integrated organic vapor/particle sampler
IPCC	Intergovernmental Panel on Climate Change
IPM	inhalable particulate matter
IPN	Inhalable Particulate Network
ISO	International Standards Organization
K	Koschmieder constant
LAI	leaf area indices
LOD	level of detection
LWC	liquid water content
LWCA	liquid water content analyzer
MAA	mineral acid anion
MAACS	Metropolitan Acid Aerosol Characterization Study
MADPro	Mountain Acid Deposition Program
MAQSIP	Multiscale Air Quality Simulation Platform
mCa	membrane-associated calcium
MDL	minimum detection level
MOUDI	micro-orifice uniform deposit impactor
MS	mass spectroscopy
MSA	methane sulfonic acid
MSA	metropolitan statistical area
mv	motor vehicle

NAAQS	National Ambient Air Quality Standards
NAMS	National Ambient Monitoring Stations
NAPAP	National Acid Precipitation Assessment Program
NARSTO	North American Research Strategy for Tropospheric Ozone
NAST	National Assessment Synthesis Team
NCEA	National Center for Environmental Assessment
NDDN	National Dry Deposition Network
NERL	National Exposure Research Laboratory
NESCAUM	Northeast States for Coordinated Air Use Management
NFRAQS	North Frontal Range Air Quality Study
NGOs	non-governmental organizations
NHAPS	National Human Activity Pattern Survey
NIOSH	National Institute for Occupational Safety and Health
NIR	near infrared radiation
NIST	National Institute of Standards and Technology
NOPL	naso-oro-pharyngo-laryngeal
NO _x	nitrogen oxides
NPP	net primary production
Nr	reactive nitrogen
NRC	National Research Council
NuCM	nutrient cycling model
OAQPS	Office of Air Quality Planning and Standards
OAR	Office of Air and Radiation
OC	organic carbon
ORD	Office of Research and Development
PAH	polynuclear aromatic hydrocarbon
PAN	peroxyacetyl nitrate
PAR	photosynthetically active radiation

PBL	planetary boundary layer
PBP	primary biological particles
PBY	Presbyterian Home
PC	particle concentrator
PC	pyrolitic carbon
PC-BOSS	Particulate Concentrator-Brigham Young University Organic Sampling System
PCA	principal component analysis
PCBs	polychlorinated biphenyls
PCDD	polychlorinated dibenzo- <i>p</i> -dioxins
PCDF	polychlorinated dibenzofurans
PCM	particle composition monitor
PEM	personal exposure monitor
PESA	proton elastic scattering analysis
PIXE	proton induced X-ray emission
PM	particulate matter
PM ₁₀₋₂₅	coarse particulate matter
PM _{2.5}	fine particulate matter
PMF	positive matrix factorization
POP	persistent organic pollutant
PRB	policy-relevant background
PTEAMS	Particle Total Exposure Assessment Methodology
PTEP	PM ₁₀ Technical Enhancement Program
PUF	polyurethane foam
PWC	precipitation-weighted concentrations
RAMS	Regional Air Monitoring Study
RAMS	Real-Time Air Monitoring System
RAS	roll-around system
RCS	Random Component Superposition

RFO	residual fuels oils
RH	relative humidity
RIVM	Directorate-General for Environmental Protection
RPM	Regional Particulate Model
RPM	respirable particulate matter
RRMS	relatively remote monitoring sites
RTP	Research Triangle Park
RUE	radiation use efficiency
SA	Sierra Anderson
SAB	Science Advisory Board
SCAQS	Southern California Air Quality Study
SCOS	Southern California Ozone Study
sd	standard deviation
sec	secondary
SEM	scanning electron microscopy
SES	sample equilibration system
SEV	Sensor Equivalent Visibility
SIP	State Implementation Plans
SLAMS	State and Local Air Monitoring Stations
SMPS	scanning mobility particle sizer
SMSAs	Standard Metropolitan Statistical Areas
SOC	semivolatile organic compounds
SoCAB	South Coast Air Basin
SOPM	secondary organic particulate matter
SP	Staff Paper
SRM	standard reference method
STN	Speciation Trends Network
SUVB	solar ultraviolet B radiation

SVOC	semivolatile organic compounds
SVM	semivolatile material
TAR	Third Assessment Report
TDMA	Tandem Differential Mobility Analyzer
TEO	trace element oxides
TEOM	tapered element oscillating microbalance
THEES	Total Human Environmental Exposure Study
TNF	tumor necrosis factor
TOFMS	aerosol time-of-flight mass spectroscopy
TOR	thermal/optical reflectance
TOT	thermal/optical transmission
TPM	thoracic particulate matter
TRXRF	total reflection X-ray fluorescence
TSP	total suspended particulates
TVOC	total volatile organic compounds
UAM-V	Urban Airshed Model Version V
UCM	unresolved complex mixture
UNEP	United Nations Environment Programme
URG	University Research Glassware
USGCRP	U.S. Global Change Research Program
VAPS	Versatile Air Pollution Samplers
VMD	volume mean diameter
VOC	volatile organic compounds
WMO	World Meteorological Organization
VR	visual range
WINS	Well Impactor Ninety-Six
WMO	World Meteorological Organization
WRAC	Wide Range Aerosol Classifier

WTA	willingness to accept
WTP	willingness to pay
XAD	polystyrene-divinyl benzene
XRF	X-ray fluorescence

EXECUTIVE SUMMARY

E.1 INTRODUCTION

The purpose of this document, Air Quality Criteria for Particulate Matter (PM AQCD), is to present air quality criteria for particulate matter (PM) in accordance with Clean Air Act (CAA) Sections 108 and 109, which govern establishment, review, and revision of U.S. National Ambient Air Quality Standards (NAAQS) as follows:

- Section 108 directs the U.S. Environmental Protection Agency (EPA) Administrator to list pollutants that may reasonably be anticipated to endanger public health or welfare and to issue air quality criteria for them. The air quality criteria are to reflect the latest scientific information useful in indicating the kind and extent of all identifiable effects on public health and welfare expected from the presence of the pollutant in ambient air.
- Section 109 directs the EPA Administrator to set and periodically revise, as appropriate, (a) primary NAAQS, which in the judgement of the Administrator, are requisite to protect public health, with an adequate margin of safety, and (b) secondary NAAQS which, in the judgement of the Administrator, are requisite to protect the public welfare from any known or anticipated adverse effects (e.g., impacts on vegetation, crops, ecosystems, visibility, climate, man-made materials, etc.).
- Section 109 of the CAA also requires periodic review and, if appropriate, revision of existing criteria and standards. Also, an independent committee of non-EPA experts, the Clean Air Scientific Advisory Committee (CASAC), is to provide the EPA Administrator advice and recommendations regarding the scientific soundness and appropriateness of criteria and NAAQS.

To meet these CAA mandates, this document assesses the latest scientific information useful in deriving criteria as scientific bases for decisions on possible revision of current PM NAAQS. A separate EPA PM Staff Paper will draw upon assessments in this document, together with technical analyses and other information, to identify alternatives for consideration by the EPA Administrator with regard to possible retention or revision of the PM NAAQS.

1 The present document is organized into a set of 10 chapters, as follows:

- 2 • This Executive Summary summarizes key points from the ensuing chapters.
- 3 • Chapter 1 provides a general introduction, including information on legislative requirements
- 4 and history of the PM NAAQS and an overview of approaches used to prepare this document.
- 5 • Chapters 2, 3 and 5 provide background information on PM atmospheric science, air quality,
- 6 and human exposure aspects to help place the succeeding discussions of PM health and
- 7 environmental effects into perspective.
- 8 • Chapter 4 deals with environmental effects of PM on vegetation and ecosystems, visibility,
- 9 man-made materials, and climate.
- 10 • Human health issues related to PM are addressed in Chapter 6 (Dosimetry); Chapter 7
- 11 (Toxicology); and Chapter 8 (Community Epidemiology).
- 12 • Chapter 9 provides an integrative synthesis of key points from the preceding chapters.

13 **E.2 AIR QUALITY AND EXPOSURE ASPECTS**

14 The document's discussion of air quality and exposure aspects considers chemistry and
15 physics of atmospheric PM; analytical techniques for measuring PM mass, size, and chemical
16 composition; sources of ambient PM in the United States; temporal/spatial variability and trends
17 in ambient U.S. PM levels; and ambient concentration-human exposure relationships. Overall,
18 the atmospheric science and air quality information provides further evidence substantiating the
19 1996 PM AQCD conclusion that distinctions between fine and coarse mode particles (in terms of
20 emission sources, formation mechanisms, atmospheric transformation, transport distances, air
 quality patterns, and exposure relationships) warrant fine and coarse PM being viewed as
 separate subclasses of ambient PM. Key findings are summarized in the next several sections.

E.2.1 Chemistry and Physics of Atmospheric Particles

- Airborne PM is not a single pollutant, but rather is a mixture of many subclasses of pollutants with each subclass containing many different chemical species. Particles suspended in the atmosphere originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. A complete description of atmospheric particles would include an accounting of the chemical composition, morphology, and size of each particle, and the relative abundance of each particle type as a function of particle size. Recent developments in single particle analysis techniques are bringing such a description closer to reality.
- Particle size distributions show that atmospheric particles exist in two classes: fine particles and coarse particles. Fine and coarse particles are defined primarily in terms of their formation mechanisms and size; they also differ in sources, chemical composition, and removal processes (see Table 2-1). Subsequent chapters show that fine and coarse particles also differ in aspects of concentration, exposure, dosimetry, toxicology, and epidemiology. These differences support the setting of separate standards for fine and coarse particles.
- Fine and coarse particles overlap in the size range between 1 and 3 μm aerodynamic diameter where ambient PM concentrations are at a minimum. Coarse particles are generally larger than this minimum and are generally formed by mechanical processes. Energy considerations limit the break-up of large mineral particles and small particle aggregates generally to a minimum size of about 1 μm in diameter. Coarse particles and coarse-mode particles are equivalent terms.
- Fine PM is derived primarily from combustion material that has volatilized and then condensed to form primary PM or from precursor gases reacting in the atmosphere to form secondary PM. New fine particles are formed by the nucleation of gas phase species; they grow by coagulation (existing particles combining) or condensation (gases condensing on existing particles). Fine particles are subdivided into accumulation, Aitkin, and nucleation modes. In earlier texts, nuclei mode referred to the size range now split into the Aitkin and nucleation modes (see Figures 2-4 and 2-5). Particles in the size range below 0.1 μm diameter are called ultrafine or nanoparticles and include the Aitkin and nucleation modes.

- 1 • $PM_{2.5}$ is an indicator for fine particles. $PM_{10-2.5}$ is an indicator for thoracic coarse particles (coarse particles capable of reaching the thoracic portion of the respiratory system – trachea, bronchi, and alveolar regions). $PM_{2.5}$ has been selected as the indicator for fine particles to include all accumulation-mode particles during high relative humidity, while recognition that it also includes some coarse-mode particles between 1 and 2.5 μm . $PM_{2.5}$ specifies a sample collected through a size-selective inlet with a specified penetration curve at 50% cut point at 2.5 μm aerodynamic diameter.
- 2 • Aerosol scientists use three different approaches or conventions in the classification of particles by size: (1) modes, based on the observed size distributions and formation mechanisms; (2) cut point, usually based on the 50% cut point of the specific sampling device, including legally specified, regulatory sizes for air quality standards; and (3) dosimetry or occupational health sizes, based on the entrance into various compartments of the respiratory system.

3

4 **E.2.2 Sources of Airborne Particles in the United States**

- 5 • Because of the complexity of the composition of ambient $PM_{2.5}$ and $PM_{10-2.5}$, sources are best discussed in terms of individual constituents of both primary and secondary $PM_{2.5}$ and $PM_{10-2.5}$. Each of these constituents can have anthropogenic and natural sources as shown in Table 3-8. Major components of fine particles are sulfates, strong acid, ammonium nitrate, organic compounds, trace elements (including metals), elemental carbon, and water.
- 6 • Primary particles are emitted directly from sources. Secondary particles are formed from atmospheric reactions of sulfur dioxide (SO_2), nitrogen oxides (NO_x), and certain organic compounds. NO reacts with ozone (O_3) to form NO_2 . SO_2 and NO_2 react with hydroxy radical (OH) during the daytime to form sulfuric and nitric acid. During the nighttime, NO_2 reacts with ozone and forms nitric acid through a sequence of reactions involving the nitrate radical (NO_3). These acids may react further with ammonia to form ammonium sulfates and nitrates. Some types of higher molecular weight organic compounds react with OH radicals, and olefinic compounds also react with ozone to form oxygenated organic compounds,

which nucleate or can condense onto existing particles. SO_2 also dissolves in cloud and fog droplets, where it may react with dissolved O_3 , H_2O_2 , or, if catalyzed by certain metals, with O_2 , yielding sulfuric acid or sulfates, that lead to PM when the droplet evaporates.

- 7
- Organic compounds constitute from 10 to 70% of dry $\text{PM}_{2.5}$ mass. Whereas the chemistry of particulate nitrate and sulfate formation has been relatively well studied, the chemistry of secondary organic particulate matter formation is especially complex. Although additional sources of secondary organic PM might still be identified, there appears to be a general consensus that biogenic compounds (monoterpenes, sesquiterpenes) and aromatic compounds (e.g., toluene and ethylbenzene) are the most significant precursors. Atmospheric transformations of the compounds, which are formed in the particle phase during the aging of particles, are still not adequately understood.
- 8
- The results of receptor modeling studies throughout the United States indicate that the combustion of fossil and biomass fuels is the major source of measured ambient $\text{PM}_{2.5}$. Fugitive dust, found mainly in the $\text{PM}_{10-2.5}$ range size, represents the largest source of measured ambient PM_{10} in many locations in the western United States. The application of any of the source apportionment techniques is still limited by the availability of source profile data. Whereas the Chemical Mass Balance approach relies directly on source profile data, solutions from the Positive Matrix Factorization technique yield profiles for the factors that contribute to PM.
- 9
- The use of organic compounds in source apportionment studies could potentially result in the attribution of PM to many more source categories than is possible using only trace elements. However, in the relatively few studies of the composition of the organic fraction of ambient particles that have been performed, typically only about 10 to 20 % of organic compounds have been quantified. The separation of contributions from diesel- and gasoline-fueled vehicles using organic marker compounds is still somewhat problematic. Additional efforts to develop protocols for extraction and analysis of organic markers are needed.
- 10

E.2.3 Atmospheric Transport and Fate of Airborne Particles

- Primary and secondary fine particles have long lifetimes in the atmosphere (days to weeks) and travel long distances (hundreds to thousands of kilometers). They tend to be uniformly distributed over urban areas and larger regions, especially in the eastern United States. As a result, they are not easily traced back to their individual sources.
- Coarse particles normally have shorter lifetimes (minutes to hours) and generally only travel short distances (<10's of km). Therefore, coarse particles tend to be unevenly distributed across urban areas and tend to have more localized effects than fine particles. However, dust storms occasionally cause long range transport of small coarse-mode particles.

E.2.4 Airborne Particle Measurement Methods

- Measurements of ambient PM mass and chemical composition are needed to determine attainment of standards; to guide progress towards attainment of a standard (including determination of source categories and validation of air quality models); and to determine health, ecological, and radiative effects. A comprehensive approach requires a combination of analytical techniques to assess (1) mass, (2) crustal and trace elements, (3) water-soluble ionic species including strong acidity, (4) elemental carbon, and (5) organic compounds.
- There are no calibration standards for suspended particle mass; therefore, the accuracy of particle mass measurements cannot be definitively determined. The precision of particle mass measurements can be determined by comparing results from collocated samplers. Intercomparisons, using different techniques and samplers of different designs, coupled with mass balance studies (relating the sum of components to the measured mass), provide a method for gaining confidence in the reliability of PM measurements.
- Mass concentration measurements with a precision of 10% or better have been obtained with collocated samplers of identical design. Field studies of EPA PM₁₀ and PM_{2.5} reference methods and reviews of field data from collocated PM₁₀ and PM_{2.5} samplers show high precision (better than $\pm 10\%$). The use of more careful techniques, including double

weighing of filters, can provide higher precision and may be needed for precise determination of $PM_{10-2.5}$ by difference.

- 10
 - Analytical techniques exist for measurement of the mass and chemical composition of PM retained on a filter (nonvolatile mass) in terms of elements (except carbon) and certain key ions (sulfate, nitrate, hydrogen, and ammonium). Acceptable measurements can be made of the total carbon retained on a filter. However, the split into organic carbon and elemental carbon depends on the operational details of the analytical methods and varies somewhat among methods. Determination of the various organic compounds in the organic carbon fraction remains a challenge.
- 11
 - Important components of atmospheric PM (particle-bound water, ammonium nitrate, and many organic compounds) are termed semivolatile because significant amounts of both the gaseous and condensed phases may exist in the atmosphere in equilibrium. Particle-bound water is not considered a pollutant. Most of the particle-bound water is removed by heating the particles or by equilibration of the collected particles at a low relative humidity (40%) for 24 hours. However, these processes also cause the loss of other semivolatile components. Semivolatile components also evaporate from the filter during sampling due to the pressure drop across the filter or due to a reduction in the atmospheric concentration during the sampling time.
- 12
 - Continuous methods must dry the PM to remove particle-bound water. If heating is used to dry the particles, more of the semivolatile components may be removed than are lost in filter sampling. Collection and retention of ammonium nitrate and semivolatile organic compounds represents a major challenge in the effort to move to continuous measurement of PM mass. The use of diffusion dryers, which dehumidify the air stream without heating, represents a promising approach. Uncertainty in the efficiency of retention of ammonium nitrate and organic compounds on filters also affects source category attribution and epidemiologic studies.

- 1 • Semivolatile organic compounds and semivolatile ammonium compounds (such as NH_4NO_3) may be lost by volatilization during sampling. Such losses may be very important in woodsmoke impacted areas for organic compounds or in agricultural and other areas where low sulfate and high ammonia lead to high NH_4NO_3 concentrations. New techniques are now in use for measurement of nitrates and new research techniques are being tested for measurement of mass of semivolatile organic compounds in PM and of the total (semivolatile plus non-volatile) PM mass. The Federal Reference Methods (FRM) for PM_{10} and $\text{PM}_{2.5}$ give precise ($\pm 10\%$) measurements of "equilibrated mass." However, the loss of semivolatile PM (ammonium nitrate and organic compounds) and the possible retention of some particle-bound water in current PM mass measurements contribute to uncertainty in the measurement of the mass of PM as it exists suspended in the atmosphere.
- 2 • Techniques are available to separate fine particles from coarse particles and collect the fine particles on a filter. No such technique exists for coarse particles. As yet, no consensus exists on the best technique for collecting a coarse particle sample for determination of mass and composition. Candidates include multistage impaction, virtual impaction, and difference (subtracting $\text{PM}_{2.5}$ mass or composition from PM_{10} mass or composition). Advances in the theory and practice of virtual impaction suggest that it should be possible to design virtual impactors with much less than the 10% of fine PM collected in the coarse PM sample, as is now the case for the dichotomous samplers used in air quality studies and with penetration curves as sharp as those used in the current FRM for $\text{PM}_{2.5}$.

3 4 **E.2.5 Ambient PM Concentrations in the U.S.**

- 5 • The recently deployed $\text{PM}_{2.5}$ FRM network has provided data for a large number of sites across the United States. The data are stored in the Aerometric Information Retrieval System (AIRS). Data have also been collected at remote sites as part of the IMPROVE and NESCAUM networks. Annual mean U.S. $\text{PM}_{2.5}$ concentrations from 1999 to 2000 range from about $5 \mu\text{g}/\text{m}^3$ to about $30 \mu\text{g}/\text{m}^3$. In the eastern United States, the data from 1999 to 2001 indicate that highest quarterly mean concentrations and maximum concentrations most often occur during the summer. In the western United States, highest quarterly mean values

and maximum values occur mainly during the winter at a number of sites although there were exceptions to these general patterns. $PM_{2.5}$ and PM_{10} concentrations in many urban areas have generally declined over the past few decades. However, they appear to have leveled off in the past few years.

- 6 • The median $PM_{2.5}$ concentration across the United States during 1999, 2000, and 2001, the first three years of operation of the $PM_{2.5}$ FRM network, was $13 \mu\text{g}/\text{m}^3$, with a 95th percentile value of $18 \mu\text{g}/\text{m}^3$. The corresponding median $PM_{10-2.5}$ concentration was $10 \mu\text{g}/\text{m}^3$, with a 95th percentile value of $21 \mu\text{g}/\text{m}^3$.
- 7 • Although $PM_{2.5}$ concentrations within a given Metropolitan Statistical Area (MSA) can be highly correlated between sites, there can still be significant differences in their concentrations. The degree of spatial uniformity in $PM_{2.5}$ concentrations and the strength of site to site correlations in urban areas varies across the country. These factors should be considered in using data obtained by the $PM_{2.5}$ FRM network to approximate community-scale human exposures, and caution should be exercised in extrapolating conclusions as to spatial uniformity or correlations obtained in one urban area to another. Limited information also suggests that the spatial variability in urban source contributions is likely to be larger than for regional source contributions to $PM_{2.5}$ and for $PM_{2.5}$, itself.
- 8 • Data for $PM_{10-2.5}$ concentrations are not as abundant as they are for $PM_{2.5}$. The difference method used in their derivation is subject to the effects of uncertainties in measuring both PM_{10} and $PM_{2.5}$. As a result, estimates of $PM_{10-2.5}$ concentrations, at times, come out as negative values, based on currently available data (e.g., in the EPA AIRS Database). In most cities where significant data is available, $PM_{10-2.5}$ is spatially less uniform than $PM_{2.5}$.
- 9 • Ambient PM contains both primary and secondary components. The results of ambient monitoring studies and receptor modeling studies indicate that $PM_{2.5}$ is dominated by secondary components in the eastern United States. General statements about the origin of OC in ambient $PM_{2.5}$ samples cannot yet be made and so the contribution of secondary components throughout the rest of the United States is still highly uncertain. Primary constituents represent a smaller but still important component of $PM_{2.5}$. Crustal materials,

which are primary constituents, constitute the largest measured fraction of $PM_{10-2.5}$ throughout the United States. Data for the concentration of bioaerosols in both the $PM_{2.5}$ and $PM_{10-2.5}$ size ranges are sparse.

- 10
- Recent but limited information about policy-relevant background concentrations have not provided sufficient evidence to warrant any changes in estimates of the annual average background concentrations given in the 1996 PM AQCD. These are: 1 to 4 $\mu g/m^3$ in the West and 2 to 5 $\mu g/m^3$ in the East for $PM_{2.5}$; and approximately 3 $\mu g/m^3$ in both the East and the West for $PM_{10-2.5}$, with a range of 0 to 9 $\mu g/m^3$ in the West and 0 to 7 $\mu g/m^3$ in the East. Such concentrations are likely to be highly variable both spatially and temporally. Further information regarding the frequency distribution of 24-hour concentrations based on analyses of observations at relatively remote monitoring sites and on source apportionment analyses has become available and can be used for selected sites.

11

12 **E.2.6 Human Exposure to PM**

- 13
- Personal exposure to PM mass or its constituents results when individuals come in contact with particulate pollutant concentrations in locations or microenvironments that they frequent during a specific period of time. Various PM exposure metrics can be defined according to its source (i.e., ambient, nonambient) and the microenvironment where exposure occurs.
- 14
- Most people spend most of their time indoors where they are exposed to indoor-generated PM and ambient PM that has infiltrated indoors.
- 15
- Indoor-generated and ambient PM differ in sources, sizes, chemical composition, and toxicity.
- 16
- The ambient PM concentration and the indoor PM concentration can be measured by outdoor and indoor monitors. The total personal exposure can be measured by a personal exposure monitor carried by the person. However, the concentrations of indoor-generated PM and

ambient PM that has infiltrated indoors and the related values of ambient and nonambient PM exposures must be estimated.

- 17 • The intercept of a regression of individual, daily values of total personal exposure on daily PM concentrations, gives the average nonambient PM exposure; and the slope gives the average attenuation factor (the ratio of ambient PM exposure to ambient PM concentration).
- 18 • Similarly, the intercept of a regression of individual, daily values of indoor PM concentration on daily ambient concentrations, gives the average concentration of indoor-generated PM; and the slope gives the average infiltration factor (concentrations of ambient PM that has infiltrated indoors/ambient PM concentration).
- 19 • The attenuation factor and the infiltration factor depend on the penetration coefficient, the fraction of ambient PM that penetrates through the walls, doors, windows, etc.; the deposition or removal rate, a measure of how rapidly PM within the indoor microenvironment is removed by deposition to surfaces or by filtration in a heating/cooling system; and the air exchange rate, a measure of how rapidly indoor air is replaced by outdoor air. The attenuation factor also depends on the fraction of time spent outdoors.
- 20 • The air exchange rate is an important variable for determining the concentration of ambient PM found indoors. It can be measured by release and measurement of an inert tracer gas indoors. The air exchange rate increases with opening of windows or doors or operation of window or attic fans. It also increases as the indoor/outdoor temperature difference increases. For closed homes, i.e., no open windows or doors, the air exchange rate does not appear to be a function of wind speed or direction.
- 21 • The penetration coefficient and the deposition rate can be estimated from measurements of outdoor and indoor concentrations under conditions when there are no indoor sources (night time or unoccupied home). These parameters are functions of particle size. The penetration coefficient is high and the deposition rate is low for accumulation mode particles (0.1 to 1.0 μm). The penetration coefficient is lower and the deposition rate is higher for ultrafine particles ($< 0.1 \mu\text{m}$) and coarse mode particles ($> 1.0 \mu\text{m}$). The attenuation factor and the

infiltration factor are higher for particles in the accumulation mode than for ultrafine or coarse particles.

- 22 • The attenuation factor and the infiltration factor will vary as the air exchange rate does, and, therefore, will vary with season and housing characteristics. These factors will increase with increased opening of windows and doors. For closed homes, these factors will increase with an increase of the indoor/outdoor temperature difference; but they do not appear to be affected by wind speed or direction.
- 23 • The regression technique is useful for finding average values of the attenuation factor and the nonambient exposure and possibly for estimating the distribution of individual, daily values of the nonambient PM exposure.
- 24 • Individual, daily values of the ambient PM exposure, the nonambient PM exposure, and the attenuation factor may be determined from individual, daily values of the total PM personal exposure and daily ambient PM concentrations by several techniques:
 - 25 – *Mass balance technique.* Direct measurement of the air exchange rate, measurement of the fraction of time spent outdoors by a diary of the subject's activity pattern, and use of the equilibrium mass balance equation for the attenuation factor with estimated values of the penetration coefficient and the deposition rate.
 - 26 – *Sulfate ratio technique.* Individual, daily values of the attenuation factor (for $PM_{2.5}$) will be given by individual, daily values of personal exposure to sulfate / the daily ambient sulfate concentration provided there are no indoor sources of sulfate and sulfate and $PM_{2.5}$ have similar particle size distributions.
 - 27 – *Recursive technique.* Indoor-generated emissions, which tend to be episodic, can be removed from a continuous record of indoor PM concentration, allowing separation of indoor-generated PM and ambient PM that has infiltrated indoors.
- 28 • In pooled studies (different subjects measured on different days), individual, daily values of total PM exposure are usually not well correlated with daily ambient PM concentrations.

In longitudinal studies (each subject measured for multiple days), individual, daily values of total PM personal exposure and daily ambient PM concentrations are highly correlated for some, but not all subjects.

- 29 • Only one study has reported estimated individual, daily values of ambient and nonambient PM exposure. Individual, daily values of total PM personal exposure and daily ambient PM concentrations were poorly correlated. However, individual, daily values of ambient PM exposure and daily ambient PM concentrations were highly correlated. Individual daily values of ambient and nonambient PM exposure were not well correlated. Individual daily values of nonambient PM exposure and daily ambient PM concentrations were also not well correlated.
- 30 • As long as the nonambient PM exposure is not correlated with the ambient PM exposure, it will not bias the estimated health effect of PM. However, the effect per $\mu\text{g}/\text{ambient PM}$ concentration will be biased low compared to the health effect per $\mu\text{g}/\text{ambient PM}$ exposure by the attenuation factor. This effect probably explains some of the heterogeneity in PM_{10} effects observed in multicity epidemiology studies, as indicated by a correlation of PM effects in different cities with air conditioning use in those cities (i.e., the higher the air conditioning use, the lower the health effect estimate per $\mu\text{g}/\text{m}^3$ of ambient PM).
- 31 • Exposure relationships also provide some insight into the issue of confounding. While the data base is small, concentrations of gaseous co-pollutants, NO_2 , O_3 , and SO_2 (and probably CO) are likely poorly correlated, and sometimes not significantly correlated, with personal exposure to the respective co-pollutant. However, they are frequently significantly correlated with both the ambient PM concentration and the ambient PM exposure. Thus, in a regression, where associations are found between gaseous co-pollutants and a health effect, it may be because they are a surrogate for PM rather than a confounder. That is, the health effect due to PM is transferred to the gaseous pollutant because of the positive correlation between the ambient concentration of the gas and the ambient PM exposure.

1 **E.3 DOSIMETRY OF PARTICULATE MATTER**

- 2 • Dosimetry establishes the relationship between PM exposure and the dose of inhaled PM
3 delivered to and retained at the target site. Deposition, clearance, translocation, and retention
4 comprise the essential elements of dosimetry.
- 5 • Dosimetric information is critical to extrapolating effects found in controlled exposure
6 studies of laboratory animals to those observed in human exposure studies and for relating
7 effects in normal healthy persons to those in potentially susceptible persons.
- 8 • Dosimetry separates the respiratory tract into three regions, extrathoracic (ET),
9 tracheobronchial (TB), and alveolar (A), based on anatomical features and particle deposition
10 and clearance phenomena that occur within each region.
- 1 • Particles in the accumulation mode size range (0.1 to $1.0 \mu\text{m } D_p$) have the lowest deposition
2 fraction in all three regions.
- 3 • Coarse and ultrafine particles have higher fractional deposition. For coarse particles,
4 fractional deposition peaks between 5 and $10 \mu\text{m } D_p$ for the TB region and 2.5 and $5 \mu\text{m } D_p$
5 for the A region.
- 6 • For ultrafine particles, fractional deposition peaks between 0.0025 and $0.005 \mu\text{m } D_p$ for the
7 TB region and between 0.01 and 0.05 for the A region.
- 8 • A significant fraction of ultrafine and coarse particles, but not particles in the accumulation-
9 mode size range, are deposited in the ET region.
- 10 • Such transport could provide a mechanism whereby particles could affect cardiovascular
1 function as reported in the epidemiologic studies
- 2 • Fractional deposition, as a function of particle size, depends on lung size, tidal volume, and
3 breathing rate. Exercising subjects receive higher doses of particles per cm^2 of lung surface
4 than subjects at rest.

- 1
 - Airway structure and physiological function vary with age. Such variations may alter the deposition patterns for inhaled particles. Airflow distribution is very uneven in diseased lungs, and deposition can be enhanced locally in areas of active ventilation. Total lung deposition is generally increased by obstructed airways so that particle deposition can be enhanced in people with chronic lung disease. Unfortunately, deposition studies in another susceptible population, the elderly, are still lacking.
- 2
 - Particles depositing on airway surfaces may be completely cleared from the respiratory tract or translocated to other sites within this system by regionally specific clearance mechanisms. Clearance is either absorptive (dissolution) or nonabsorptive (transport of intact particles). Deposited particles may be dissolved in body fluids, taken up by phagocytic cells, or transported by the mucociliary system. Retained particles tend to be small ($< 2.5 \mu\text{m}$) and poorly soluble (e.g., silica, metals). Ultrafine particles can be rapidly cleared from the lungs into the systemic circulation where they can be transported to extrapulmonary regions.
- 3
 - Tracheobronchial clearance has both a fast and a slow component. In the fast phase particles deposited in the TB region clear out rapidly during the first several hours and continue to clear out for 24 hours. A small remaining portion may clear out over several days (slow phase). Translocation of poorly soluble PM to the lymph nodes takes a few days and is more rapid for smaller ($< 2 \mu\text{m}$) particles; elimination rates of these retained particles are on the order of years. People with COPD have increased particle retention partly because of increased initial deposition and impaired mucociliary clearance and use cough to augment mucociliary clearance.
- 4
 - Alveolar clearance takes months to years. Particles may be taken up by alveolar macrophages within 24 hours, but some phagocytosed macrophages translocate into the interstitium or lymphatics whereas some remain on the alveolar surface. Penetration of uningested particles into the interstitium increases with increasing particle load and results in increased translocation to lymph nodes.
- 5
 - Acute effects of PM are probably best related to deposited dose; whereas chronic effects may be related to cumulative or retained dose. Retention of particles is a function of deposition

site, clearance of particles by macrophages or the mucociliary system, and particle characteristics, especially solubility. Chronic effects may also arise from recurring cycles of pulmonary injury and repair.

- Computational models allow calculation of fractional deposition and dose per cm² of lung surface as a function of particle size and respiratory parameters for humans and some animals (including the laboratory rat). Such calculations can be used to predict the exposures needed to produce comparable doses for animal to human extrapolation. Computational models have been improved in recent years but experimental validation of model predictions is still required.

E.4 TOXICOLOGY OF PARTICULATE MATTER IN HUMANS AND LABORATORY ANIMALS

E.4.1 Health Effects of Specific PM Components

- There is relatively little new information on the effects of acid aerosols, and the conclusions of the 1996 PM AQCD, i.e., Air Quality Criteria for Particulate Matter (U.S. Environmental Protection Agency, 1996a), are unchanged. It was previously concluded that acid aerosols cause little or no change in pulmonary function in healthy subjects, but asthmatics may develop small changes in pulmonary function. Although pulmonary effects of acid aerosols have been the subject of extensive research in past decades, the cardiovascular effects of acid aerosols have received little attention and should not be ruled out as possible mediators of PM health effects.
- Health effects of particle-associated soluble metals have been demonstrated by in vivo and in vitro studies using residual oil fly ash (ROFA) or soluble transition metals. Although there are some uncertainties about differential effects of one transition metal versus another, water soluble metals leached from ROFA or ambient filter extracts have been shown consistently (albeit at high concentrations) to cause cell injury and inflammatory changes in vitro and in vivo.

- 1 • Even though it is clear that combustion particles that have a high content of soluble metals can cause lung injury and even death in compromised animals and correlate well with epidemiologic findings in some cases (e.g., Utah Valley Studies), it has not been fully established that the small quantities of metals associated with ambient PM are sufficient to cause health effects. Moreover, it cannot be assumed that metals are the only or the primary toxic component of ambient PM, rather than there possibly being many different toxic agents contributing to ambient PM health effects.
- 2 • There is growing toxicological evidence that diesel exhaust particles exacerbate the allergic response to inhaled antigens. The organic fraction of diesel exhaust has been linked to eosinophil degranulation and induction of cytokine production, suggesting that the organic constituents of diesel PM are the responsible part for the immune effects. It is not known whether the adjuvant-like activity of diesel PM is unique or whether other combustion particles have similar effects. It is important to compare the immune effects of other source-specific emissions, as well as concentrated ambient PM, to diesel PM to determine the extent to which exposure to diesel exhaust may contribute to the incidence and severity of allergic rhinitis and asthma.
- 3 • Published research on the acute effects of particle-associated organic carbon constituents is conspicuous by its relative absence, except for diesel exhaust particles.
- 4 • Studies with ultrafine particles have demonstrated a significantly greater inflammatory response than that seen with fine particles of the same chemical composition at similar mass doses. In other more limited studies, ultrafines also have generated greater oxidative stress in experimental animals. However, when the particle surface area is used as a dose metric, the inflammatory response to both fine and ultrafine particles may be basically the same. Thus, it may be the higher surface area of ultrafine particles is the important factors contributing to health effects.
- 5 • Concentrated ambient particle (CAPS) studies should be among the most relevant in helping to understand the characteristics of PM producing toxicity, susceptibility of individuals to PM, and the underlying mechanisms. Studies have used collected urban PM for intratracheal administration to healthy and compromised animals. Despite the difficulties in extrapolating

from the bolus delivery used in such studies, they have provided strong evidence that the chemical composition of ambient particles can have a major influence on toxicity.

- 6 • Ambient particle concentrators, that concentrate particles in situ, provide particles for inhalation studies. The concentration of particles without collection avoids the changes in size and composition that occur during collection during collection and resuspension. Studies with inhaled CAPs have observed cardiopulmonary changes in rodents and dogs at high concentrations of PM between 0.15 and 2.5 μm diameter. A new generation of ambient particle concentrators that allow separation and concentration of coarse-mode, accumulation-mode, and ultrafine particle separately will permit the direct toxicological comparison of these various ambient particle sizes.
- 7 • Recent studies support the conclusion of the 1996 PM AQCD, which stated that bioaerosols, at concentrations present in the ambient environment, cannot account for the reported health effects of ambient PM. However, it is possible that bioaerosols could contribute to the health effects of PM.

8

9 **E.4.2 Mechanisms of Action**

10 **E.4.2.1 Cardiovascular Effects**

- 11 • Changes in heart rate, heart rate variability, and conductance associated with ambient PM exposure have been reported in animal studies, in several human panel studies, and in a reanalysis of data from the MONICA study. Some of these studies included endpoints related to respiratory effects but few significant adverse respiratory changes were detected. This raises the possibility that ambient PM may have effects on the heart that are independent of adverse changes in the lung.
- 12 • Inhaled particulate matter affects the heart by uptake of particles into the circulation or release of a soluble substances into the circulation.
- 13 • Inhaled particulate matter affects autonomic control of the heart and cardiovascular system.

14

15

1 E.4.2.2 Respiratory Effects

- 2 • Particularly compelling evidence pointing towards ambient PM causing lung injury and inflammation derives from the study of ambient PM materials on filter extracts collected from community air monitors before, during the temporary closing of a steel mill in Utah Valley, and after its reopening. Intratracheal instillation of filter extract materials in human volunteers provoked greater lung inflammatory responses for materials obtained before and after the temporary closing versus that collected during the plant closing. Further, the instillation in rats of extract materials from before and after the plant closing resulted in a 50% increase in air way hyperresponsiveness to acetylcholine compared to 17 or 25% increases with saline or extract materials for the period when the plant was closed, respectively. Analysis of the extract materials revealed notably greater quantities of metals for when the plant was opened suggesting that such metals (e.g., Cu, Zn, Fe, Pb, As, Mn, Ni) may be important contributors to the pulmonary toxicity observed in the controlled exposure studies, as well as to health effects shown epidemiologically to vary with PM exposures of Utah Valley residents before, during, and after the steel mill closing.
- 3 • Still other toxicological studies point towards lung injury and inflammation being associated with exposure of lung tissue to complex combustion-related PM materials, with metals again being likely contributors. Rats with SO₂-induced bronchitis and monocrotaline-treated rats have been reported to have a greater inflammatory response to concentrated ambient PM than normal rats. These studies suggest that exacerbation of respiratory disease by ambient PM may be caused in part by lung injury and inflammation.
- 4 • Particulate air pollution causes increased susceptibility to respiratory infections. Exposure of rats to ROFA and *L. monocytogenes*, a bacterial pathogen, led rats treated with saline or *L. monocytogenes* in the absence of ROFA. Preexposure of rats to ROFA significantly enhanced injury and delayed the pulmonary clearance of a subsequent challenge of *L. monocytogenes*, when compared to saline-treated control rats. Acute exposure to ROFA appeared to slow pulmonary clearance of *L. monocytogenes* and to alter AM function. Such changes could lead to increased susceptibility to lung infection in exposed populations.

- 1 • Particulate air pollution increases airway reactivity and exacerbates asthma. Diesel
particulate matter (DPM) has been shown to increase production of antigen-specific IgE in
mice and humans. In vitro studies have suggested that the organic fraction of DPM is
involved in the increased IgE production. ROFA leachate also has been shown to enhance
antigen-specific airway reactivity in mice, indicating that soluble metals can also enhance an
allergic response.

2 3 **E.4.2.3 Systemic Effects Secondary to Lung Injury**

- 4 • Lung injury from inhaled PM causes impairment of oxygenation and increased work of
breathing that adversely affects the heart.
- 5 • Lung inflammation and cytokine production cause adverse systemic hemodynamic effects.
- 6 • Lung inflammation from inhaled PM causes increased blood coagulability that increases the
risk of heart attacks and strokes.
- 7 • Interaction of PM with the lung affects hematopoiesis.

8 9 **E.4.3 Susceptibility**

- 10 • Older animals or animals with certain types of compromised health, either genetic or
induced, are more susceptible to instilled or inhaled particles, although the increased animal-
to-animal variability in these models has created greater uncertainty for the interpretation of
the findings. Moreover, because PM seems to affect broad categories of disease states,
ranging from cardiac arrhythmias to pulmonary infection, it can be difficult to know what
disease models to use in evaluating the biological plausibility of adverse health effects of
PM. Nevertheless, particularly interesting new findings point toward ambient PM
exacerbation of allergic airway hyperresponsiveness and/or antigen-induced immune
responses. Both metals and diesel particles have been implicated, with an expanding array of
new studies showing DPM in particular as being effective in exacerbating allergic asthma
responses.

E.5 EPIDEMIOLOGY OF HUMAN HEALTH EFFECTS ASSOCIATED WITH AMBIENT PARTICULATE MATTER

Chapter 8 of this document assesses the extensive PM epidemiologic data base that has become newly available since the 1996 PM AQCD. The most important types of additions to the epidemiologic database beyond that assessed in the 1996 PM AQCD include the following:

- New multi-city studies on a variety of endpoints which provide more precise estimates of the average PM effect sizes than most smaller-scale individual city studies;
- More studies of various health endpoints using ambient PM_{10} and/or closely related mass concentration indices (e.g., PM_{13} and PM_7), which substantially lessen the need to rely on non-gravimetric indices (e.g., BS or CoH);
- New studies evaluating relationships of a variety of health endpoints to the ambient PM coarse fraction ($PM_{10-2.5}$), the ambient fine-particle fraction ($PM_{2.5}$), and even ambient ultrafine particles measures ($PM_{0.1}$ and smaller), using direct mass measurements and/or estimated from site-specific calibrations;
- A few new studies in which the relationship of some health endpoints to ambient particle number concentrations were evaluated;
- Many new studies which evaluated the sensitivity of estimated PM effects to the inclusion of gaseous co-pollutants in the model;
- Preliminary attempts to evaluate the effects combinations or mixtures of air pollutants including PM components, based on factor analysis or source profiles;
- Numerous new studies of cardiovascular endpoints, with particular emphasis on assessment of cardiovascular risk factors as well as symptoms;
- Additional new studies on asthma and other respiratory conditions potentially exacerbated by PM exposure;
- New analyses of lung cancer associations with long-term exposures to ambient PM;

- New studies of infants and children as a potentially susceptible population.

In addition, Chapter 8 discusses statistical issues posed by use of General Additive Mode (GAM) analyses involving default convergence criteria in widely used commercially-available software employed in time-series analyses of ambient PM-health effects relationship reported in a few published studies assessed in the 1996 PM AQCD and in numerous more recent studies assessed in the present PM AQCD. This includes discussion of the following key points:

- Use of GAM analyses with default convergence criteria (GAM default) has variable impacts on PM effect size estimates from study to study, depending on many factors (numbers of observations, numbers of potential effect modifiers or potential confounders included, specific “smoothing” approaches used to control for their effects, numbers of degrees of freedom used, etc.). The effect of GAM (default) use tends most often to be some (unusually only slight) overestimation of the PM effect size compared to results obtained with use of GAM with stringent convergence criteria or other appropriate modeling approaches, e.g., general linear models (GLM).
- The results of EPA-encouraged reanalyses of a number of (> 35) of important PM time-series analyses comparing PM effect sizes and standard error (confidence interval) estimates from GAM (default) analyses versus GAM (stringent) or other appropriate statistical approaches (GLM). These reanalyses appear in a Health Effects Institute Special Report (HEI, 2003) that includes not only short communications on the GAM reanalyses by the original investigators, but also commentaries on the reanalyses and their implications for interpreting the PM time-series analyses results by a special peer-review panel convened by HEI at EPA’s request.

E.5.2 Key Epidemiologic Findings

The epidemiologic studies discussed in Chapter 8 demonstrate biologically-plausible responses in humans exposed at ambient concentrations. These observational study findings are further enhanced by supportive findings of causal studies from other scientific disciplines (dosimetry, toxicology, etc.), in which other factors could be experimentally controlled, as

discussed in Chapters 6 and 7. The most salient findings derived from the PM epidemiologic studies include the following:

- A large and reasonably convincing body of epidemiology evidence confirms earlier associations between short- and long-term ambient PM_{10} exposures (inferred from stationary community air monitor measures) and mortality/morbidity effects and suggest that PM_{10} (or one or more PM_{10} components) is a probable contributing cause of adverse human health effects.
- There appears to be some spatial heterogeneity in city-specific excess risk estimates for the relationships between short-term ambient PM_{10} concentrations and acute health effects. The reasons for such variation in effects estimates are not well understood at this time but do not negate ambient PM's likely causative contribution to observed PM-mortality and/or morbidity associations in many locations. Possible factors contributing to the apparent heterogeneity include geographic differences in air pollution mixtures, composition of PM components, and personal and sociodemographic factors affecting PM exposure (such as use of air conditioners, education, and so on).
- A growing body of epidemiologic studies confirm associations between short- and long-term ambient $PM_{2.5}$ exposures (inferred from stationary air monitor measures) and adverse health effects and suggest that $PM_{2.5}$ (or one or more $PM_{2.5}$ components) is a probable contributing cause of observed PM-associated health effects. Some new epidemiologic findings also suggest that health effects are associated with mass or number concentrations of ultrafine (nuclei-mode) particles, but not necessarily more so than for other ambient fine PM components.
- A smaller body of evidence appears to support an association between short-term ambient thoracic coarse fraction ($PM_{10-2.5}$) exposures (inferred from stationary air monitor measures) and short-term health effects in epidemiologic studies. This suggests that $PM_{10-2.5}$, or some constituent component(s) of $PM_{10-2.5}$, may be a contributory cause of adverse health effects in some locations. Reasons for differences among findings on coarse-particle health effects reported for different cities are still poorly understood, but several of the locations where

significant $PM_{10-2.5}$ effects have been observed (e.g., Phoenix, Mexico City, Santiago) tend to be in drier climates and may have contributions to observed effects due to higher levels of organic particles from biogenic processes (endotoxins, molds, etc.) during warm months. Other studies suggest that particles of crustal origin are generally unlikely to exert notable health effects under most ambient exposure conditions. Also, in some western U.S. cities where $PM_{10-2.5}$ is a large part of PM_{10} , the relationship between hospital admissions and PM_{10} may be an indicator of response to coarse thoracic particles from wood burning.

- 7 • Long-term PM exposure durations, on the order of months to years, as well as on the order of a few days, are statistically associated with serious human health effects (indexed by mortality, hospital admissions/medical visits, etc.). More chronic PM exposures, on the order of years or decades, appear to be associated with life shortening well beyond that accounted for by the simple accumulation of the more acute effects of short-term PM exposures (on the order of a few days). Substantial uncertainties remain regarding the magnitude of and mechanisms underlying chronic health effects of long-term PM exposures and the relationship between chronic exposure and acute responses to short-term exposure.
- 8 • Recent investigations of the public health implications of such chronic PM exposure-mortality effect estimates were also reviewed. Life table calculations by Brunekreef (1997) found that relatively small differences in long-term exposure to airborne PM of ambient origin can have substantial effects on life expectancy. For example, a calculation for the 1969-71 life table for U.S. white males indicated that a chronic exposure increase of $10 \mu g/m^3$ PM was associated with a reduction of 1.3 years for the entire population's life expectancy at age 25. Also, new evidence of associations of PM exposure with infant mortality and/or intrauterine growth retardation and consequent increase risk for many serious health conditions associated with low birth weight, if further substantiated, would imply that life shortening in the entire population from long-term PM exposure could well be significantly larger than that estimated by Brunekreef (1997).
- 9 • Considerable coherence exists among effect size estimates for ambient PM health effects. For example, results derived from several multi-city studies, based on pooled analyses of

data combined across multiple cities (thought to yield the most precise estimates of mean effect size), show the percent excess total (non-accidental) deaths estimated per 50 $\mu\text{g}/\text{m}^3$ increase in 24-h PM_{10} to be ~1.4% in the 90 largest U.S. cities with the estimate for the Northeast being the largest (approximately twice the nationwide estimate); ~3.4% in 10 large U.S. cities; ~3.6% in the 8 largest Canadian cities; and ~3.0% in western European cities. These combined estimates are consistent with the range of PM_{10} estimates previously reported in the 1996 PM AQCD. These and excess risk estimates from many other individual-city studies, generally falling in the range of ca. 1.5 to 8.0% per 50 $\mu\text{g}/\text{m}^3$ 24-h PM_{10} increment, also comport well with numerous new studies confirming increased cause-specific cardiovascular- and respiratory-related mortality. They are also coherent with larger effect sizes reported for cardiovascular and respiratory hospital admissions and visits, as would be expected for these morbidity endpoints versus those for PM_{10} -related mortality.

- 10 • Several independent panel studies (but not all) that evaluated temporal associations between PM exposures and measures of heart beat rhythm in elderly subjects provide generally consistent indications of decreased heart rate variability (HRV) being associated with ambient PM exposure (decreased HRV being an indicator of increased risk for serious cardiovascular outcomes, e.g., heart attacks). Other studies point toward changes in blood characteristics (e.g., C-reactive protein levels) related to increased risk of ischemic heart disease also being associated with ambient PM exposures. However, these heart rhythm and blood characteristics findings should currently be viewed as providing only limited or preliminary support for PM-related cardiovascular effects.
- 11 • Notable new evidence now exists which substantiates positive associations between ambient PM concentrations and increased respiratory-related hospital admissions, emergency department, and other medical visits, particularly in relation to PM_{10} levels. Of much interest are new findings tending to implicate not only fine particle components but also coarse thoracic (e.g., $\text{PM}_{10-2.5}$) particles as likely contributing to exacerbation of asthma conditions. Also of much interest are emerging new findings indicative of likely increased occurrence of chronic bronchitis in association with (especially chronic) PM exposure. Also of particular interest are reanalyses or extensions of earlier prospective cohort studies of

long-term ambient PM exposure effects which demonstrate substantial evidence for association of increased lung cancer risk with such PM exposures, especially exposure to fine PM or its subcomponents.

- 12
 - One major methodological issue affecting epidemiologic studies of both short-term and long-term PM exposure effects is that ambient PM of varying size ranges is typically found in association with other air pollutants, including gaseous criteria pollutants (e.g., O₃, NO₂, SO₂, CO), air toxics, and/or bioaerosols. Available statistical methods for assessing potential confounding arising from these associations may not yet be fully adequate. The inclusion of multiple pollutants often produces statistically unstable estimates. Omission of other pollutants may incorrectly attribute their independent effects to PM. Second-stage regression methods may have certain pitfalls that have not yet been fully evaluated. Much progress in sorting out relative contributions of ambient PM components versus other co-pollutants is nevertheless being made and, overall, tends to substantiate that observed PM effects are at least partly due to ambient PM acting alone or in the presence of other covarying gaseous pollutants. However, the statistical association of health effects with PM acting alone or with other pollutants should not be taken as an indicator of a lack of effect of the other pollutants.
- 13
 - It is possible that differences in observed health effects will be found to depend on site-specific differences in chemical and physical composition characteristics of ambient particles and on factors affecting exposure (such as air conditioning) as well as on differences in PM mass concentration. For example, epidemiologic Utah Valley studies showed that PM₁₀ particles, known to be richer in metals during exposure periods while the steel mill was operating, were more highly associated with adverse health effects than was PM₁₀ during the PM exposure reduction while the steel mill was closed. In contrast, PM₁₀ or PM_{2.5} was relatively higher in crustal particles during windblown dust episodes in Spokane and in three central Utah sites than at other times, but was not associated with higher total mortality. These differences require more research that may become more feasible as the PM_{2.5} sampling network produces air quality data related to speciated samples.

- 1 • The above reasons suggest it is inadvisable to pool PM epidemiologic studies for different locations or time periods, with different population sub-groups, or different health endpoints (as is often done in "meta-analyses"), without careful assessment of potential causes and consequences of these differences and appropriate caveating of results. Published multi-city analyses using common data bases, measurement methods, analytical strategies, and extensive independent external review (as carried out in the APHEA and NMMAPS studies) are useful. Pooled analyses of more diverse collections of independent studies of different cities, using varying methodology and/or data quality or representativeness, are likely less credible and should not, in general, be used without careful assessment of their underlying scientific comparability.
- 2 • It may be possible that different PM size components or particles with different composition or sources produce effects by different mechanisms manifested at different lags or that different preexisting conditions may lead to different delays between exposure and effect. Thus, although maximum effect sizes for PM effects have often been reported for 0-1 day lags, evidence is also beginning to suggest that more consideration should be given to lags of several days. Also, if it is considered that all health effects occurring at different lag days are all real effects, so that the risks for each lag day should be additive, then overall risks may exist that are higher than implied by maximum estimates for any particular single or two-day lags. In that case, multi-day averages or distributed lag models may provide more accurate estimate of the total impact of PM on the population.
- 3 • Certain classes of ambient particles may be distinctly less toxic than others and may not exert human health effects at typical ambient exposure concentrations or only under special circumstances. Coarse thoracic particles of crustal origin, for example, may be relatively non-toxic under most circumstances compared to those of combustion origin such as wood burning. However, crustal particles may be sufficiently toxic to cause human health effects under some conditions; resuspended crustal particles, for example, may carry toxic trace elements and other components from previously deposited fine PM, e.g., metals from smelters (Phoenix) or steel mills (Steubenville, Utah Valley), PAH's from automobile exhaust, or pesticides from administration to agricultural lands. Likewise, fine particles

from different sources have different effect sizes. More research is needed to identify conditions under which one or another class of particles may cause little or no adverse health effects, as well as conditions under which different classes of particles may cause relatively more notable effects.

- 4 • Certain epidemiologic evidence from “intervention studies” suggests that reducing ambient PM_{10} concentrations may reduce a variety of health effects on a time scale from a few days to a few months, as found in epidemiologic studies of “natural experiments” such as in the Utah Valley, and supported by toxicology studies using particles extracts from ambient community sampling filters from the Utah Valley. Recent studies in Germany and in the Czech Republic also tend to support a hypothesis that reductions in particle-related air pollution are associated with reductions in the incidence of adverse health effects.
- 5 • Studies that combine the features of cross-sectional and cohort studies provide the best evidence for chronic effects of PM exposure. Gauderman et al. (2000; 2002) have found significant decreases in lung function growth related to PM_{10} levels using these techniques.
- 6 • Adverse health effects in children reported in a limited number of more recent studies are emerging as an important area of more concern than was the case in the 1996 PM AQCD. Unfortunately, relatively little is known about the relationship of PM to the most serious health endpoints, neonatal and infant mortality, emergency hospital admissions and mortality in older children, as well as low birth weight and preterm birth.
- 7 • Little is yet known about involvement of PM exposure in the progression from less serious childhood conditions, such as asthma and respiratory symptoms, to more serious disease endpoints later in life. This is an important health issue because childhood illness or death may cost a very large number of productive life-years.
- 8 • Lastly, new epidemiologic studies of ambient PM associations with increased non-hospital medical visits (physician visits) and asthma effects suggest likely much larger health effects and costs to society due to ambient PM than just those indexed by mortality and/or hospital admissions/visits.

E.6 ENVIRONMENTAL EFFECTS OF PM

E.6.1 Vegetation and Ecosystem Effects

- Deposition of particulate matter from the atmosphere has the potential to alter ecosystem structure and function. Human existence on this planet depends on the essential life-support services that ecosystem structure and functions provide. Concern has risen in recent years regarding the consequences of changing the biological diversity of ecosystems because human activities are creating disturbances that are altering the structure (complexity and stability) and functioning (producing changes in the processes of energy and water flow and nutrient cycling) of ecosystems.
- Human-induced changes in biotic diversity and alterations in the structure and ecosystems processes are the two most dramatic ecological trends in the past century. Biodiversity encompasses all levels of biological organization, including individuals, populations, species, and ecosystems. For this reason, there is a need to understand the effects of PM deposition on vegetation and ecosystems and biodiversity.
- Ecosystem functions maintain clean water, pure air, biodiversity, and impart the following benefits: fixation of solar energy, absorption and breakdown of pollutants, cycling of nutrients, binding of soil, degradation of organic wastes, maintenance of a balance of atmospheric gases, regulation of radiation balance, and climate.
- The deposition of PM onto vegetation and soil, depending on its chemical composition (acid/base, trace metal, or nutrients, e.g., nitrates or sulfates), can produce direct or indirect responses within an ecosystem.
- Ecosystem response to pollutant deposition is a direct function of the level of sensitivity of the ecosystem and its ability to ameliorate resulting changes. Changes in ecosystem structural patterns and the functioning of ecological processes must be scaled in both time and space and propagated to the more complex levels of community interaction to produce observable ecosystem changes.

- 1 • The major effect of atmospheric PM on ecosystems is indirect and occurs through the deposition of nitrates and sulfates and the acidifying effects of the associated H^+ ion in wet and dry deposition in the soil environment. In the soil, they have the potential to inhibit nutrient uptake, alter the ecological processes of energy flow and nutrient cycling, change ecosystem structure, and affect ecosystem biodiversity. Most nitrate is not deposited or measured as PM but is a combination of wet and dry deposition.
- 2 • The soil environment, one of the most dynamic sites of biological interaction, is inhabited by communities of bacteria, fungi, and actinomycetes. Bacteria, as essential components of the nitrogen and sulfur cycles, and fungi in the uptake of mineral nutrients play an important role in plant nutrition. Their actions make these elements available for plant uptake. Fungi form mycorrhizae, a mutualistic symbiotic relationship with plant roots that is integral to the uptake of mineral nutrients. Changes in the soil environment resulting from deposition of nitrates and sulfates that alter the role of the bacteria in the nutrient cycles and mycorrhizal fungi in making minerals available for plant utilization, determine plant and, ultimately, ecosystem response.
- 3 • Although nitrogen as molecular nitrogen (N_2) is the most abundant element in the atmosphere, it only becomes available to support plant growth after its conversion into reactive forms. In nature, nitrogen may be divided into two groups: reactive (Nr) and nonreactive (N_2). Reactive nitrogen or Nr includes the inorganic reduced forms of nitrogen (e.g., ammonia [NH_3] and ammonium [NH_4^+]), inorganic oxidized forms (e.g., nitrogen oxides [NO_x], nitric acid [HNO_3], nitrous oxide [N_2O], and nitrate [NO_3^-]), and organic compounds (e.g., urea, amine, proteins, and nucleic acids).
- 4 • Reactive nitrogen can be widely dispersed and accumulate in the environment when the rates of its formation exceed the rates of removal via denitrification. As a result of human food production, it is now accumulating in the environment on all spatial scales – local, regional and global; and its creation and accumulation is projected to increase as per capita use of resources by human populations increases.

- 1
 - The major changes in the nitrogen cycle can be both beneficial and detrimental to the health and welfare of humans and ecosystems. The cascade of environmental effects resulting from reactive nitrogen accumulation include the following: (1) production of tropospheric ozone and aerosols that induce human health and ecosystem problems; (2) increases in the productivity in forests and grasslands followed by decreases wherever Nr deposition increases significantly and exceeds critical thresholds; (3) reactive nitrogen additions probably decrease biodiversity in many natural habitats; (4) in association with sulfur is responsible for acidification and loss of biodiversity in lakes and streams in many regions of the world; (5) eutrophication, hypoxia, loss of biodiversity, and habitat degradation in coastal ecosystems. [Eutrophication is now considered the biggest pollution problem in coastal waters.], and (6) contributes to global climate change and stratospheric ozone depletion, which can in turn affect ecosystems and human health.
- 2
 - “Nitrogen saturation” results when reactive nitrogen concentrations exceed the capacity of a system to utilize it. Saturation implies that some resource other than nitrogen is limiting biotic function. Water and phosphorus for plants and carbon for microorganisms are most likely to be the secondary limiting factors. The appearance of nitrogen in soil solution is an early symptom of excess nitrogen. In the final stage, disruption of ecosystem structure becomes visible.
- 3
 - Possible ecosystem responses to nitrogen saturation include (1) a permanent increase in foliar nitrogen and reduced foliar phosphorus and lignin caused by the lower availability of carbon, phosphorus, and water; (2) reduced productivity in conifer stands because of disruptions of physiological function; (3) decreased root biomass and increased nitrification and nitrate leaching; (4) reduced soil fertility, resulting from increased cation leaching and increased nitrate and aluminum concentrations in streams, (5) decreased water quality, and (6) changes in soil microbial communities from predominantly fungal (mycorrhizal) communities to those dominated by bacteria during saturation.

- 1 • Intensive research over nearly a decade indicates that, although the soils of most North American forests are nitrogen limited, severe symptoms of nitrogen saturation have been observed in the high-elevation, non-aggrading spruce-fir ecosystems in the Appalachian Mountains; the eastern hardwood watersheds at the Fernow Experimental Forest near Parsons, WV; forests in southern California; the southwestern Sierra Nevada in Central California; and the Front Range in northern Colorado. The mixed conifer forest and chaparral watershed with high smog exposure in the Los Angeles Air Basin exhibit the highest stream water NO_3^- concentrations in wilderness areas of North America.
- 2 • Increases in soil nitrogen play a selective role in ecosystems. Plant succession patterns and biodiversity are affected significantly by chronic nitrogen additions in some North American ecosystems. Long-term nitrogen fertilization studies in both New England and Europe suggest that some forests receiving chronic inputs of nitrogen may decline in productivity and experience greater mortality. Declining coniferous forest stands with slow nitrogen cycling may be replaced by deciduous fast-growing forests that rapidly cycle nitrogen.
- 3 • In experimental studies nitrogen deposition over a 12-year period Minnesota grasslands dominated by native warm-season grasses shifted to low-diversity mixtures dominated by cool-season grasses.
- 4 • Excess nitrogen inputs to unmanaged heathlands in the Netherlands has resulted in nitrophilous grass species replacing slower growing heath species. Over the past several decades the composition of plants in the forest herb layers has been shifting toward species commonly found in nitrogen-rich areas. It also was observed that the fruiting bodies of mycorrhizal fungi had decreased in number, indicating that formation of mycorrhizae were affected.
- 5 • Soil nitrogen enrichment of the soil significantly alters the composition and richness of the arbuscular mycorrhizal fungal community and markedly decreases overall diversity of the mycorrhizal community. Decline in the coastal sage scrub in southern California was directly linked to the decline of arbuscular mycorrhizal fungal community.

- 1
 - The effects of excessive deposition of nitrogen, particularly NH_3 and NH_4^+ , have led to changes in Dutch heathlands via: (1) acidification of the soil and the loss of cations of K^+ , Ca^{2+} and Mg^{2+} ; and (2) nitrogen enrichment, which results in increased plant growth rates and altered competitive relationships. Alteration of any of a number of parameters (e.g., increased nitrogen) can alter ecosystem structure and function.
- 2
 - Notable effects of excess nitrogen deposition have been observed with regard to aquatic systems. Atmospheric nitrogen deposition onto soils in watershed areas feeding into estuarine sound complexes (e.g., the Pamlico Sound of North Carolina) appear to contribute to excess nitrogen flows in runoff (especially during and after heavy rainfall events such as hurricanes) from agricultural practices or other uses (e.g., fertilization of lawns or gardens). Massive influxes of such nitrogen into watersheds and sounds can lead to algae blooms, which, upon degradation, deplete oxygen and cause extensive fish kills and damage to commercial fish and sea food harvesting.
- 3
 - Acidic precipitation, a critical environmental stress that affects forest landscapes and aquatic ecosystems in North America, Europe, and Asia, is linked to the effects associated with the deposition of Nr and sulfates and the associated hydrogen ion. The resulting soil acidity can lead to nutrient deficiencies and to high aluminum-to-nutrient ratios that limit uptake of calcium and magnesium and create a nutrient deficiency adversely affect tree growth. Calcium is essential in the formation of wood and the maintenance of the primary plant tissues necessary for tree growth.
- 4
 - The critical loads concept is useful for estimating the amounts of pollutants (e.g., reactive nitrogen and acidic precipitation) that sensitive ecosystems can absorb on a sustained basis without experiencing measurable degradation. The estimation of ecosystem critical loads requires an understanding of how an ecosystem will respond to different loading rates in the long term and can be of special value for ecosystems receiving chronic deposition of Nr and sulfur independently and as acidic deposition when in combination.

- 1 • The biological effect of PM is determined by the amount deposited during the wet and dry deposition onto the plant surfaces or soil in the vicinity of the roots. The three major routes involved are (1) precipitation scavenging in which particles are deposited in rain and snow; (2) occult (fog, cloud water, and mist interception); and (3) dry deposition, a much slower, yet more continuous removal to place surfaces.
- 2 • Few heavy metals (e.g., copper, nickel, zinc) have been documented to have direct phytotoxicity under field conditions. Ecosystems immediately downwind of major emissions sources such as power generating, industrial, or urban complexes can receive locally heavy inputs. Heavy metal accumulation in the richly organic forest floor where biological activity is greatest by affecting litter decomposition present the greatest potential for influencing nutrient cycling. The presence of cadmium, copper and nickel have been observed to affect the symbiotic activity of fungi, bacteria, and actinomycetes.
- 3 • Phytochelatins produced by plants as a response to sublethal concentrations of heavy metals, are indicators of metal stress and can be used to indicate that heavy metals are involved in forest decline. Increasing concentrations of phytochelatins with increasing altitude, and their increases across regions that show increased levels of forest injury, have implicated them in forest decline.
- 4 • Secondary organics formed in the atmosphere have been variously subsumed under the following terms: toxic substances, pesticides, hazardous air pollutants (HAPS), air toxics, semivolatile organic compounds (SOCs), and persistent organic pollutants (POPS). Such substances are controlled under CAA Sect. 112, Hazardous Air Pollutants (not as criteria pollutants controlled by NAAQS under CAA Sections 108 and 109). Their possible effects on humans and ecosystems are discussed in many other government documents and publications. They are noted in this document because, in the atmosphere, many of the chemical compounds are partitioned between gas and particle phases and are deposited as particulate matter. As particles, they become airborne and can be distributed over a wide area and affect remote ecosystems. Some are also of concern to humans because they may reach toxic levels in food chains of both animals and humans; whereas others may tend to maintain or decrease some toxicity as they move through the food chain.

1 E.6.2 Visibility

2 Chapter 4 of this document includes information supplementary to several other significant
3 reviews of the science of visibility, including the 1991 report of the National Acid Precipitation
4 Assessment Program, the National Research Council's *Protecting Visibility in National Parks*
5 *and Wilderness Areas* (1993), and EPA's 1995 *Interim Findings on the Status of Visibility*
6 *Research*. The following points are made in Chapter 4 and/or in the above referenced
7 documents.

- 8 • The relationships between air quality and visibility are well understood. Ambient fine
particles are the major cause of visibility impairment. Significant scientific evidence exists
showing that reducing fine particle concentrations will improve visibility.
- 9 • The National Research Council defines visibility qualitatively as "the degree to which the
atmosphere is transparent to visible light." This definition may be expressed quantitatively in
terms of contrast transmittance. The EPA has defined visibility impairment as a reduction in
visual range (the farthest distance at which a large black object can be distinguished against
the horizontal sky is the visual range) and/or atmospheric discoloration.
- 10 • Light, as it passes through the atmosphere from a scene to an observer, is both scattered and
absorbed. The rate of loss of transmitted light intensity with distance is measured by the
light-extinction coefficient, which may be expressed as the sum of the coefficients for:
(a) light scattering due to gases; (b) light scattering due to particles; (c) light absorption by
gases, and; (d) light absorption by particles. Light scattering by particles is the major
component of light extinction. Light absorption by gases is almost entirely due to NO₂, and is
typically significant only near NO₂ sources. Light absorption by particles is primarily caused
by elemental carbon.
- 11 • Light scattering efficiency depends on particle size, falling off rapidly for particles below
0.3 or above 1.0 μm in diameter. Therefore, particles in the accumulation mode (of the fine
particle mode) are most effective in scattering light and are more important in visibility
degradation than either nuclei-mode or coarse-mode particles. Light absorption is not a
strong function of particle size. Under exceptional circumstances, such as dust storms, coarse
particles can dominate scattering.

- 1 • In addition to reducing the intensity of light carrying information about a scene (transmitted radiance), particles also scatter light into the observer's view. This extraneous light, called air light or path radiance, carries no information about the scene. The competition between these two sources of light, expressed as the ratio of transmitted radiance from the scene to path radiance, determines the contrast transmittance and the visual quality of the view.
- 2 • Visibility at any location is affected by air quality and non-air quality related effects. The visibility effects of atmospheric constituents are dependant upon not just the mass of pollutants, but on the size distribution and refractive index of particles, which are strongly influenced by relative humidity. Non-air quality effects include the angle between the sun and the observer's sight path, location of clouds, and reflectivity of the ground. These effects are independent of effects due to changes in atmospheric constituents. Lighting and scene effects can be accounted for by defining a range of these effects when estimating visibility changes due to air quality influences.
- 3 • The relationship between air pollution and the appearance of a scenic view is well understood. Models exist that, given an adequate description of the air quality and non-air quality variables, can produce a simulated photograph that accurately depicts a cloud-free scene as it would appear to a human observer.
- 4 • There are several potential quantitative indicators of visibility, including: (a) fine particle mass and composition (fine particle mass alone provides less of both types of information); (b) scattering by dried ambient particles; (c) scattering by particles under ambient conditions; (d) extinction (calculated from measurements of scattering plus absorption); (e) light extinction measured directly; and (f) contrast transmittance.
- 5 • A new index, the deciview (dv), is now being used as a quantitative measure of haziness. It is related to the light extinction coefficient, b_{ext} , by $Haziness (dv) = 10 \ln(b_{ext}/10 Mn)$. The deciview is more nearly linearly related to perceived changes in haze level than either visual range or light extinction. A change of 1 or 2 dv in uniform haze under many viewing conditions will be seen as a small but noticeable change in the appearance of a scene regardless of the initial haze condition.

- 1 • Visibility in the United States is best in the western, intermountain region. Visibility
impairment or haziness is greatest in the eastern United States and southern California.
Haziness in the eastern United States is caused primarily by atmospheric sulfate. Haziness in
southern California is primarily caused by nitrate and organic PM. Nitrates contribute about
40% to the total light extinction in southern California. Nitrates account for 10 to 20% of the
total extinction in other areas of the United States.
- 2 • Organics are the second largest contributors to light extinction in most areas in the United
States. Organic carbon is the greatest cause of light extinction in the Pacific Northwest,
Oregon, Idaho, and Montana, accounting for 40 to 45% of the total extinction. Organic
carbon contributes between 15 to 20% to the total extinction in most of the western United
States and 20 to 30% in the remaining areas of the United States.
- 3 • Light absorption by carbon is relatively insignificant but is highest in the Pacific Northwest
(up to 15%) and in the eastern United States (3%).
- 4 • High dust concentrations transported from southern California and the subtropics have
contributed to regional haze in the Grand Canyon and other Class I areas in the southwestern
United States.

6 **E.6.3 Particulate Matter-Related Effects on Materials**

7 Atmospheric PM and SO₂ exert effects on materials that are related both to aesthetic appeal
8 and physical damage. Studies have demonstrated particles, primarily consisting of carbonaceous
9 compounds, cause soiling of commonly used building materials and culturally important items
10 such as statues and works of art. Physical damage from the dry deposition of SO₂, particles, and
11 the absorption or adsorption of corrosive agents on deposited particles can also result in the
12 acceleration of the weathering of manmade building and naturally occurring cultural materials.

- 13 • The natural process of metal corrosion from exposure to environmental elements (wind,
moisture, sun, temperature fluctuations, etc.) is enhanced by exposure to anthropogenic
pollutants, in particular SO₂.

- 1 • Dry deposition of SO₂ enhances the effects of environmental elements on calcereous stones (limestone, marble, and carbonated cemented) by converting the calcium carbonate (calcite) in the stone to calcium sulphate dihydrate (gypsum). The rate of deterioration is determined by the SO₂ concentration, the stone's permeability and moisture content, and the deposition rate.
- 2 • Sulfur dioxide limits the life expectancy of paints by causing discoloration, loss of gloss, and loss of thickness of the paint film layer.
- 3 • A significant detrimental effect of particulate pollution is the soiling of painted surfaces and other building materials. Soiling is a degradation process requiring remediation by cleaning or washing, and depending on the soiled surface, repainting. Soiling decreases the reflectance of a material and reduces the transmission of light through transparent materials. Soiling may reduce the life usefulness of the material soiled.

4 5 **E.6.4 Effects of Atmospheric Particulate Matter on Global Warming** 6 **Processes and Transmission of Solar Ultraviolet Radiation**

- 7 • The physical processes (i.e., scattering and absorption) responsible for airborne particle effects on transmission of solar visible and ultraviolet radiation are the same as those responsible for visibility degradation. Scattering of solar radiation back to space and absorption of solar radiation determine the effects of an aerosol layer on solar radiation.
- 8 • Atmospheric particles greatly complicate projections of future trends in global warming processes because of emissions of greenhouse gases; consequent increases in global mean temperature; resulting changes in regional and local weather patterns; and mainly deleterious (but some beneficial) location-specific human health and environmental effects. The body of available evidence, ranging from satellite to in situ measurements of aerosol effects on radiation receipts and cloud properties, is strongly indicative of an important role in climate for aerosols. This role, however, is poorly quantified. No significant advances have been made in reducing the uncertainties assigned to forcing estimates provided by the IPCC for aerosol-related forcing, especially for black carbon-containing aerosol. The IPCC

characterizes the scientific understanding of greenhouse gas-related forcing as “high” in contrast to that for aerosol, which it describes as “low” to “very low.”

- 9 • Quantification of the effect of anthropogenic aerosol on hydrological cycles requires more information than is presently available regarding ecosystems responses to reduced solar radiation and other changes occurring in the climate system. However, several global scale studies indicate that aerosol cooling alone can slow down the hydrological cycle, while cooling plus the nucleation of additional cloud droplets can dramatically reduce precipitation rates.
- 10 • In addition to direct climate effects through the scattering and absorption of solar radiation, particles also exert indirect effects on climate by serving as cloud condensation nuclei, thus affecting the abundance and vertical distribution of clouds. The direct and indirect effects of particles appear to have significantly offset global warming effects caused by the buildup of greenhouse gases on a globally-averaged basis. However, because the lifetime of particles is much shorter than that required for complete mixing within the Northern Hemisphere, the climate effects of particles generally are felt much less homogeneously than are the effects of long-lived greenhouse gases.
- 11 • Any effort to model the impacts of local alterations in particle concentrations on projected global climate change or consequent local and regional weather patterns would be subject to considerable uncertainty.
- 12 • Atmospheric particles also complicate estimation of potential future impacts on human health and the environment projected as possible to occur because of increased transmission of solar ultraviolet radiation (UV-B) through the Earth’s atmosphere, secondary to stratospheric ozone depletion due to anthropogenic emissions of chlorofluorocarbons (CFCs), halons, and certain other gases. The transmission of solar UV-B radiation is affected strongly by atmospheric particles. Measured attenuations of UV-B under hazy conditions range up to 37% of the incoming solar radiation. Measurements relating variations in PM mass directly to UV-B transmission are lacking.

- 1 • Particles also can affect the rates of photochemical reactions occurring in the atmosphere,
e.g., those involved in catalyzing tropospheric ozone formation. Depending on the amount of
absorbing substances in the particles, photolysis rates either can be increased or decreased.
Thus, atmospheric particle effects on UV-B radiation, which vary depending on size and
composition of particles, can differ substantially over different geographic areas and from
season to season over the same area. Any projection of effects of location-specific airborne
PM alterations on increased atmospheric transmission of solar UV radiation (and associated
potential human health or environmental effects) due to stratospheric ozone-depletion would,
therefore, also be subject to considerable uncertainty.

2 3 **E.7 KEY CONCLUSIONS**

- 4 • Epidemiologic studies show consistent positive associations of exposure to ambient PM with
health effects, including mortality and morbidity. The observed associations of ambient PM
exposure with health effects must take into account the effects of other environmental or
demographic factors, depending on whether the effects are acute or chronic. Effect-size
estimates for PM-attributable excess relative risk for a given health outcome vary somewhat
depending on specific analytic models used, but nevertheless have shown reasonable
quantitative consistency across different studies.
- 5 • Issues surrounding potential bias in PM risk estimates from time-series studies using
generalized additive models analyses and default convergence criteria were recently raised.
Reanalyses of some important studies were included in an HEI Special Report (2003) that
generally confirmed that PM effect estimates generally decline somewhat when using more
stringent convergence criteria, as compared to the default GAM analyses, with the new
estimates being well within confidence intervals of the original estimates. Overall, the
absolute effect was relatively small, and the basic direction of effect and conclusions
regarding the significance of the PM effect on mortality and hospital admissions remained
unchanged in these analyses when the GAM convergence requirement was made more
stringent. A modeling issue of particular importance highlighted by HEI (2003) is the

sensitivity of all models to the degrees of freedom allotted to potentially confounding weather variables and time. The HEI panel recommended further exploration of the sensitivity of these studies to a wider range of alternative degrees of smoothing and to alternative specifications of weather variables in time-series models.

- 6
 - Individuals with cardiovascular or pulmonary disease, especially if they are elderly, are more likely to suffer severe health effects (mortality or hospitalization) related to PM exposure than are healthy young adults. Children and asthmatics are also susceptible to certain PM effects, e.g., increased respiratory symptoms and decreased lung function. Smokers also constitute a population group at increased risk for ambient PM exposure effects.
- 7
 - Daily ambient fine particle concentrations measured at a community air-monitoring site are useful surrogates for daily personal exposures to ambient fine particles. This is consistent, for example, with observed high correlations of personal sulfate exposures with ambient sulfate concentrations. The relationship between personal exposure to thoracic coarse particles and the ambient concentration of thoracic coarse fraction particles is not as strong, making effects due to coarse fraction particles harder to detect in epidemiologic studies.
- 8
 - Development of a comprehensive biologically based exposure-dose-response model to aid health risk assessment requires further dosimetry data characterizing differences among species in percent deposition and regional deposition patterns including differences in inhalability, airway geometry, and clearance rates. More information is also needed on mechanism(s) of clearance, pathological processes affecting deposition and clearance of particles, and factors influencing the response(s) of respiratory tract tissues to particle burden.
- 9
 - The percent deposition and regional patterns of deposition depend strongly on particle size. Percent deposition is higher in smaller lungs (children; women), during exercise, and in the functioning parts of the lungs in people with compromised lungs (e.g., those with chronic obstructive lung disease).
- 10
 - Estimation of public health impacts of ambient airborne particle exposures in the United States would most credibly combine information on exposure-response relationships derived

for particular U.S. urban areas, in combination with estimates of exposures to ambient particle concentrations for the general population and/or specific susceptible subgroups (e.g., the elderly) those particular areas. At this time, risk assessment is necessarily limited to use of available information from concentration-response relationships relating ambient concentrations to health effects in populations. In view of geographic differences in ambient PM mixtures and demographics, broad generalization of some single "best estimate" of relative risk for a given increment in concentration of a given particle indicator (e.g., PM₁₀, PM_{2.5}, etc.) would be subject to much uncertainty.

- 11 • Toxicological studies of PM using controlled inhalation exposure of humans and laboratory animals, intratracheal instillation in humans and animals, and exposure of human and animal cells grown in culture find numerous biological effects which may be related to adverse health effects. Newer studies are finding different biological effects for a variety of different particle components. Newer studies also are beginning to identify biological mechanisms whereby PM deposited in the lung can produce adverse effects on the cardiovascular and respiratory systems.
- 12 • Epidemiologic studies indicate increased health risks associated with exposure to PM, alone or in combination with other air pollutants. PM-related increases in individual health risks are small, but likely significant from an overall public health perspective because of the large numbers of individuals in susceptible risk groups that are exposed to ambient PM.
- 13 • Numerous new studies, including multicity studies, continue to show a consistent association of PM₁₀ exposure with mortality and various morbidity endpoints, thus substantiating the relationship of PM exposure with various health effects. However, some new studies using PM_{2.5} as an indicator find higher statistical significance and higher excess risk for PM_{2.5} compared to PM₁₀. Several studies have also observed statistically associations of PM_{10-2.5} with health effects.
- 14 • Epidemiologic studies, in which factors identified with source categories or individual chemical components of PM have been used as indicators, also show significant associations

with nitrates, sulfates, various indicators of elemental carbon, the organic component of PM, and some elements. PM-related source category factors, such as regional sulfate, vehicular traffic, fossil fuel combustion, vegetative combustion, and oil burning have also been found to be significantly associated with mortality.

- 15 • Data from multicity studies, comparisons of effects found in single and multiple regressions, exposure relationships, and toxicity suggest that the gaseous co-pollutants (CO, NO₃, SO₂, O₃) are not responsible for the relationships observed with PM indicators in community, time-series epidemiology. This does not, however, necessarily imply lack of an independent association of gaseous co-pollutants with health effects.
- 16 • Fine and thoracic coarse PM, indexed respectively by PM_{2.5} and PM_{10-2.5}, should be considered as separate subclasses of PM. Considerations of emissions sources, atmospheric chemistry, physical behavior, exposure relationships, respiratory deposition, toxicologic findings, and epidemiologic observations argue for monitoring fine and thoracic coarse particles separately.
- 17 • Assessment of health risk in epidemiologic studies of ambient air pollutants, including PM, has relied largely on studies that focus on changes in health risks that occur in relation to normal changes in ambient air pollutant concentrations. Further evidence of the effects of air pollution on health may be deduced from intervention studies, i.e., studies of changes in health effects that occur when air pollution concentrations have been temporarily or permanently reduced through regulatory action, industrial shutdown, or other intervening factor(s). Only a few epidemiologic intervention studies are available; however, taken together, these studies lend confidence that further reduction of ambient air pollution exposures in the U.S. would reduce both respiratory and cardiovascular health effects. Available studies also give reason to expect that further reductions in both particulate and gaseous air pollutants would benefit health. Furthermore, experimental studies of Utah Valley filter extracts points to PM-associated metals as a likely cause or promoter of at least some of the health disorders associated with ambient PM.

- 1 • The overall weight of evidence, based on information concerning PM exposure, dosimetry, toxicology, and epidemiology, supports the conclusion that PM, especially fine PM, is the primary contributor to a variety of adverse health effects associated with air pollution. However, difficult technical issues still remain in further separating the effects of fine and coarse particles and in delineating respective contributions of PM acting along or in combination with gaseous co-pollutants in increasing risks of health effects anticipated to occur in response to exposures to contemporary particle-containing ambient air mixes in the United States.

REFERENCES

- Brunekreef, B. (1997) Air pollution and life expectancy: is there a relation? *Occup. Environ. Med.* 54: 781-784.
- Health Effects Institute. (2003) Revised analyses of time-series studies of air pollution and health. Boston, MA: Health Effects Institute; special report. Available: <http://www.healtheffects.org/Pubs/TimeSeries.pdf> [27 June 2003].
- Intergovernmental Panel on Climate Change (IPCC). (2001a) Climate change 2001: the scientific basis. Contribution of working group I to the third assessment report of the Intergovernmental Panel on Climate Change. Cambridge, United Kingdom: Cambridge University Press.
- Intergovernmental Panel on Climate Change (IPCC). (2001b) Climate change 2001: impacts, adaptation, and vulnerability. Contribution of working group II to the third assessment report of the Intergovernmental Panel on Climate Change. Cambridge, United Kingdom: Cambridge University Press.
- National Acid Precipitation Assessment Program. (1991) National Acid Precipitation Assessment Program 1990 integrated assessment report. Washington, DC: National Acid Precipitation Assessment Program.
- National Research Council. (1993) Protecting visibility in national parks and wilderness areas. Washington, DC: National Academy Press. 3v.
- United Nations Environment Programme (UNEP). (1998) Environmental effects of ozone depletion: 1998 assessment. *J. Photochem. Photobiol. B* 46: 1-4.
- United Nations Environment Programme (UNEP). (2000) Environmental effects of ozone depletion: interim summary. Available at: <http://www.gcio.org/ozone/unep2000summary.html> [9 April 2002].
- U.S. Code. (1991) Clean Air Act, §108, air quality criteria and control techniques, §109, national ambient air quality standards. U. S. C. 42: §§7408-7409.
- U.S. Environmental Protection Agency. (1995) Interim findings on the status of visibility research. Research Triangle Park, NC: Office of Research and Development; report no. EPA/600/R-95/021.
- U.S. Environmental Protection Agency. (1996) Air quality criteria for particulate matter. Research Triangle Park, NC: National Center for Environmental Assessment-RTP Office; report nos. EPA/600/P-95/001aF-cF. 3v.
- World Meteorological Organization (WMO). (1999) Scientific assessment of ozone depletion: 1998. Geneva, Switzerland: World Meteorological Organization, Global Ozone and Monitoring Project; report no. 44.

1. INTRODUCTION

This document is an update of "Air Quality Criteria for Particulate Matter" published by the U.S. Environmental Protection Agency (EPA) in 1996, and it will serve as the basis for Congressionally-mandated periodic review of the National Ambient Air Quality Standards (NAAQS) for particulate matter (PM). The present document critically assesses the latest scientific information relative to determining the health and welfare effects associated with the presence of various concentrations of PM in ambient air. The document builds upon the assessment in the previous 1996 EPA Air Quality Criteria Document for Particulate Matter (PM AQCD) by focusing on assessment and integration of information most relevant to PM NAAQS criteria development, based on pertinent peer-reviewed literature published or accepted for publication mainly through April 2002. This introductory chapter presents a brief summary of legislative requirements and history of the PM NAAQS, provides an overview of issues addressed and procedures utilized in the preparation of the present document, and provides orientation to the general organizational structure of the document.

1.1 LEGISLATIVE REQUIREMENTS

As indicated in U.S. Code (1991), the U.S. Clean Air Act (CAA), Sections 108 and 109 (42 U.S.C. Sections 7408 and 7409) govern the establishment, review, and revision of National Ambient Air Quality Standards (NAAQS). Section 108(a) directs the EPA Administrator to list pollutants, which, in the Administrator's judgement, cause or contribute to air pollution which may reasonably be anticipated to endanger either public health or welfare and to issue air quality criteria for them. The air quality criteria are to reflect the latest scientific information useful in indicating the kind and extent of all identifiable effects on public health and welfare that may be expected from the presence of the pollutant in ambient air.

Section 109 directs the Administrator of EPA to propose and promulgate "primary" and "secondary" NAAQS for pollutants identified under Section 108. Section 109(b)(1) defines a primary standard as a level of air quality, the attainment and maintenance of which, in the judgement of the Administrator, based on the criteria and allowing for an adequate margin of

1 safety, is requisite to protect the public health. Section 109(b)(2) defines a secondary standard as
2 one which, in the judgement of the Administrator, based on the criteria, is requisite to protect
3 public welfare from any known or anticipated adverse effects associated with the presence of
4 such pollutants. Welfare effects, defined in Section 302(h), include, but are not limited to,
5 effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather,
6 visibility and climate, damage to and deterioration of property, and hazards to transportation, as
7 well as effects on economic values and personal comfort and well-being. Section 109(d)(1)
8 requires periodic review and, as appropriate, revision of existing criteria and standards.
9 Section 109(d)(2) requires an independent committee of non-EPA experts, the Clean Air
10 Scientific Advisory Committee (CASAC), to provide advice and recommendations to the EPA
11 Administrator regarding the scientific soundness and appropriateness of criteria and NAAQS for
12 PM and other "criteria air pollutants" (i.e., ozone, nitrogen dioxide, sulfur oxides, carbon
13 monoxide, lead) regulated under CAA Sections 108-109.
14
15

16 **1.2 HISTORY OF PREVIOUS PM CRITERIA AND NAAQS REVIEWS**

17 "Particulate matter" is the generic term for a broad class of physically and chemically
18 diverse substances that exist in ambient air as discrete particles (liquid droplets or solids) over a
19 wide range of sizes. These airborne particles originate from a variety of stationary and mobile
20 sources. Primary particles are emitted directly into ambient air; whereas secondary particles are
21 formed in the atmosphere by transformation of gaseous emissions such as sulfur oxides (SO_x),
22 nitrogen oxides (NO_x), and volatile organic compounds (VOCs). The physical and chemical
23 properties of PM vary greatly with time, region, meteorology, and source category, thus
24 complicating assessment of ambient PM health and welfare effects. Particles in ambient air are
25 usually distributed bimodally in two somewhat overlapping size categories: (1) fine (diameter
26 generally less than 2.5 mm) and (2) coarse (diameter generally greater than 1.0 μm). Particles in
27 these two size fractions tend to differ in terms of formation mechanisms, sources of origin,
28 composition, and behavior in the atmosphere and human respiratory tract.

29 EPA first promulgated primary and secondary NAAQS for PM on April 30, 1971 (Federal
30 Register, 1971). These standards measured PM as "total suspended particulate" (TSP), which
31 refers to ambient PM up to a nominal size of 25 to 45 micrometers (μm). The primary standards

1 for PM (measured as TSP) were 260 $\mu\text{g}/\text{m}^3$ (24-h average), not to be exceeded more than once
2 per year, and 75 $\mu\text{g}/\text{m}^3$ (annual geometric mean). The secondary standard (measured as TSP)
3 was 150 $\mu\text{g}/\text{m}^3$ (24-h average), not to be exceeded more than once per year.

4 EPA completed the next review of PM air quality criteria and standards in July 1987,
5 revising the 1971 standards to protect against adverse health effects of inhalable airborne
6 particles which can be deposited in the lower (thoracic) regions of the human respiratory tract,
7 with "PM₁₀" as the indicator (i.e., those particles collected by a sampler with a specified
8 penetration curve yielding an upper 50% cut-point of 10- μm aerodynamic diameter (Federal
9 Register, 1987). EPA established identical primary and secondary PM₁₀ standards for two
10 averaging times: 150 $\mu\text{g}/\text{m}^3$ (24-h average), with no more than one expected exceedance per
11 year and 50 $\mu\text{g}/\text{m}^3$ (expected annual arithmetic mean), averaged over three years.

12 13 **1.2.1 The 1997 PM NAAQS Revision**

14 The last previous review of the air quality criteria and standards for PM was initiated in
15 April 1994 by EPA announcing its intention to develop revised Air Quality Criteria for
16 Particulate Matter. Several workshops were held by EPA's Environmental Criteria and
17 Assessment Office in Research Triangle Park, NC (ECAO-RTP) in November 1994 and January
18 1995 to discuss important new health effects information useful in preparing initial PM AQCD
19 draft materials. Also, plans for review of the PM criteria and standards under a highly
20 accelerated, court-ordered schedule were presented by EPA at a public meeting of the CASAC in
21 December 1994. A court order entered in *American Lung Association v. Browner*, CIV-93-643-
22 TUC-ACM (U.S. District Court of Arizona, 1995), as subsequently modified, required
23 publication of EPA's final decision on the review of the PM NAAQS by July 19, 1997.

24 Several external review drafts of the revised PM AQCD were prepared by the RTP
25 Division of EPA's newly created National Center for Environmental Assessment (i.e., by
26 NCEA-RTP, the successor office to ECAO-RTP), and each were made available for public
27 comment followed by CASAC review (at public meetings held in August 1995, December 1995,
28 and February 1996). The CASAC came to closure on its review of the PM AQCD in early 1996,
29 advising the EPA Administrator in a March 15, 1996 closure letter (Wolff, 1996) that "although
30 our understanding of the health effects of PM is far from complete, a revised Criteria Document
31 which incorporates the Panel's latest comments will provide an adequate review of the available

1 scientific data and relevant studies of PM.” Revisions made in response to public and CASAC
2 comments were then incorporated by NCEA-RTP, as appropriate, into the final 1996 PM AQCD
3 (U.S. Environmental Protection Agency, 1996a). A PM Staff Paper (SP), prepared by the Office
4 of Air Quality Planning and Standards (OAQPS) within EPA’s Office of Air and Radiation
5 (OAR), drew upon the 1996 PM AQCD and other exposure and risk assessments to pose options
6 for PM NAAQS decisions. Drafts of the PM SP also underwent public comment and CASAC
7 review, with consequent revision into the final 1996 PM SP (U.S. Environmental Protection
8 Agency, 1996b).

9 The 1996 PM AQCD and the 1997 PM SP (U.S. Environmental Protection Agency,
10 1997a,b) provide detailed information on atmospheric formation, ambient concentrations, and
11 health effects of ambient air PM, as well as quantitative estimates of human health risks
12 associated with exposure to ambient PM. The principal focus of these documents was on recent
13 epidemiologic evidence reporting associations between ambient concentrations of PM and a
14 range of serious health effects. Special attention was given to several size-specific classes of
15 particles, including PM_{10} and the principal fractions of PM_{10} , referred to as the fine ($PM_{2.5}$) and
16 coarse ($PM_{10-2.5}$) fractions. $PM_{2.5}$ refers to those particles collected by samplers having
17 penetration curves yielding an upper 50% cut point of 2.5 μm aerodynamic diameter. $PM_{10-2.5}$
18 refers to those particles in an aggregate sample having an upper 50% cut point of 10 μm and a
19 lower 50% cut point of 2.5 μm aerodynamic diameter. In other words, the coarse fraction
20 ($PM_{10-2.5}$) refers to the inhalable particles that remain if fine ($PM_{2.5}$) particles are removed from a
21 sample of PM_{10} particles. As discussed in the 1996 PM AQCD, fine and coarse fraction particles
22 can be differentiated by their sources and formation processes and by their chemical and
23 physical properties, including behavior in the atmosphere.

24 Taking into account information and assessments presented in the 1996 PM AQCD and
25 PM SP, advice and recommendations of CASAC, and public comments received on proposed
26 revisions to the PM NAAQS published in December 1996 (Federal Register, 1996), the EPA
27 Administrator promulgated significant revisions to the PM NAAQS in July 1997 (Federal
28 Register, 1997). In that decision, the PM NAAQS were revised in several respects. While it was
29 determined that the PM NAAQS should continue to focus on particles less than or equal to
30 10 μm in diameter, it was also determined that the fine and coarse fractions of PM_{10} should be
31 considered separately. New standards were added, using $PM_{2.5}$ as the indicator for fine particles,

1 and PM₁₀ standards were retained for the purpose of regulating coarse-fraction particles. Two
2 new PM_{2.5} standards were set: an annual standard of 15 µg/m³, based on the 3-year average of
3 annual arithmetic mean PM_{2.5} concentrations from single or multiple community-oriented
4 monitors; and a 24-hour standard of 65 µg/m³, based on the 3-year average of the 98th percentile
5 of 24-hour PM_{2.5} concentrations at each population-oriented monitor within an area. To continue
6 to address coarse-fraction particles, the annual PM₁₀ standard was retained, and the form, but not
7 the level, of the 24-hour PM₁₀ standard was revised to be based on the 99th percentile of 24-hour
8 PM₁₀ concentrations at each monitor in an area. The secondary standards were revised by
9 making them identical in all respects to the primary standards.

10 Following promulgation of the revised PM NAAQS, legal challenges were filed by a large
11 number of parties, addressing a broad range of issues. In May 1998, the U.S. Court of Appeals
12 for the District of Columbia Circuit issued an initial opinion that upheld EPA's decision to
13 establish fine particle standards, holding that such standards were amply justified by the growing
14 body of empirical evidence demonstrating a relationship between fine particle pollution and
15 adverse health effects. American Trucking Associations v. Browner, 175 F. 3d 1027, 1055-56
16 (D.C. Cir. 1999) (rehearing granted in part and denied in part, 195 F. 3d 4 (D.C. Cir. 1999b),
17 affirmed in part and reversed in part, Whitman v. American Trucking Associations, 531 U.S. 457
18 (2001). Further, the court found "ample support" for EPA's decision to regulate coarse fraction
19 particles, although it vacated the revisions to the 1987 PM₁₀ standards on the basis of PM₁₀ being
20 a "poorly matched indicator for coarse particulate pollution" because PM₁₀ includes fine
21 particles. *Id.* at 1053-55. As a result of this aspect of the court's ruling, which EPA did not
22 appeal, the 1987 PM₁₀ standards remain in effect.

23 In addition, the court broadly held that EPA's approach to establishing the level of the
24 standards in its 1997 decisions on both the PM and ozone NAAQS (which were promulgated on
25 the same day and considered together by the court in this aspect of its opinion) effected "an
26 unconstitutional delegation of legislative authority." *Id.* at 1034-40. EPA appealed this aspect of
27 the court's ruling to the United States Supreme Court. In February 2001, the U.S. Supreme
28 Court unanimously reversed the Court of Appeals' ruling on the constitutional issue, and sent the
29 case back to the Court of Appeals for resolution of any remaining issues that had not been
30 addressed in that court's earlier rulings. Whitman v. American Trucking Associations, 531 U.S.
31 457, 475-76 (2001). In March 2002, the Court of Appeals rejected all remaining challenges to

1 the standards, finding that the 1997 PM_{2.5} standards were reasonably supported by the record and
2 were not "arbitrary or capricious." American Trucking Associations v. EPA, 283 F. 3d 355,
3 369-72 (D.C. Cir. 2002). Thus, the 1997 PM_{2.5} standards are in effect.
4

5 **1.2.2 Coordinated Particulate Matter Research Program**

6 Shortly after promulgation of the 1997 PM NAAQS decisions, NCEA-RTP published a
7 PM Health Risk Research Needs Document (U.S. Environmental Protection Agency, 1998a) that
8 identified research needed to improve scientific information supporting future reviews of the PM
9 NAAQS. The document provided a foundation for PM research coordination among Federal
10 agencies and other research organizations and also provided input to later National Research
11 Council (NRC) deliberations on PM research. The Office of Research and Development (ORD)
12 of EPA also moved quickly to broaden its ongoing PM research activities by developing, in
13 partnership with other Federal agencies, a coordinated interagency PM research program. This
14 interagency program has and continues to focus mainly on expanding scientific knowledge of
15 ambient PM exposure and health effects, as well as including development of improved
16 monitoring methods and cost-effective mitigation strategies. The interagency effort also
17 promotes substantially expanded coordination with other research organizations, including the
18 Health Effects Institute (HEI) and other state-, university-, and industry-sponsored research
19 groups. Beginning in the fall of 1997, public participation was and continues to be encouraged
20 through workshops and review of EPA's PM Research Program documentation.

21 In response to Congressional requirements in EPA's Fiscal Year 1998 Appropriation, the
22 NRC established its Committee on Research Priorities for Airborne Particulate Matter in January
23 1998. This NRC PM Research Committee's charge is to identify the most important research
24 priorities relevant to setting PM NAAQS, to develop a conceptual plan for PM research, and to
25 monitor EPA's research progress toward improved understanding of the relationship between
26 PM and public health. The Committee issued its first report in early 1998 (National Research
27 Council, 1998), a second one in 1999 (National Research Council, 1999), and a third one in 2001
28 (National Research Council, 2001). In the above-noted series of reports, the NRC PM Research
29 Committee recommended that expanded PM research efforts be planned and carried out in
30 relation to a general conceptual framework as shown in Figure 1-1. That framework essentially
31 calls for research aimed at: (a) identifying sources of airborne particles or gaseous precursor

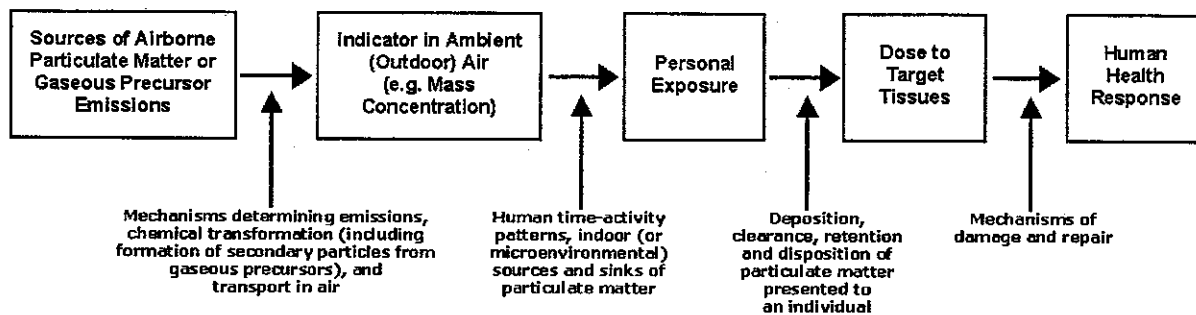


Figure 1-1. A general framework for integrating particulate-matter research. Note that this figure is not intended to represent a framework for research management. Such a framework would include multiple pathways for the flow of information.

Source: National Research Council (2001).

emissions and characterization of processes involved in atmospheric transformation, transport, and fate of ambient PM; (b) delineation of temporal and spatial patterns of air quality indicators (e.g., $PM_{2.5}$, $PM_{10-2.5}$, PM_{10} mass concentrations) of ambient PM and apportionment of observed variations in such ambient PM indicators to various emission sources; (c) characterization of human exposures to ambient PM as one important component of total personal exposure to particles, as modified by time-activity patterns and varying microenvironmental exposure to particles of indoor or ambient origin; (d) characterization of resulting respiratory tract deposition, clearance, retention, and disposition of inhaled particles, as determinants of dose to target tissues (e.g., locally in the lungs or via systemic translocation to the heart or other organs); (e) delineation of mechanisms of damage and repair plausibly leading to (f) human health responses, as extrapolated from or quantified by experimental animal or human exposure (toxicology) studies and/or observational (epidemiology) studies.

Research conducted under a PM Research Program structured in relation to the conceptual framework shown in Figure 1-1 would be expected (a) to reduce key scientific uncertainties regarding interrelationships between PM sources, ambient concentrations, exposures, dose to target tissues, and resulting health effects and (b) thereby improve the scientific underpinnings for both current and future periodic PM NAAQS reviews. Table 1-1 highlights some types of key uncertainties identified by the NRC PM Research Committee in relation to elements of the

**TABLE 1-1. KEY SCIENTIFIC UNCERTAINTIES RELATED TO THE
SOURCE-TO-RESPONSE FRAMEWORK**

Source	→	Concentration (or other indicator)
<ul style="list-style-type: none"> • Contribution of various emission sources to ambient and indoor particulate matter concentrations • Relative contribution of various sources to the most toxic components of particulate matter 		
Concentration (indicator)	→	Exposure
<ul style="list-style-type: none"> • Relationship between ambient (indoor) particulate matter and the composition of particles to which people are exposed • Contribution of ambient particulate matter to total personal exposure for: <ul style="list-style-type: none"> - Susceptible subpopulations - General population • Variation in relationship of ambient particulate matter concentrations to human exposure by place • Variation in contribution of ambient particulate matter concentrations to total human exposure over time • Covariance of particulate matter exposures with exposures to other pollutants • Relationships between outdoor ambient and personal exposures for particulate matter and co-pollutants 		
Exposure	→	Dose
<ul style="list-style-type: none"> • Relationship between inhaled concentration and dose of particulate matter and constituents at the tissue level in susceptible subjects <ul style="list-style-type: none"> - Asthma - Chronic obstructive pulmonary disease (COPD) - Heart disease - Age: infants and elderly - Others 		
Dose	→	Response
<ul style="list-style-type: none"> • Mechanisms linking morbidity and mortality to particulate matter dose to or via the lungs <ul style="list-style-type: none"> - Inflammation - Host defenses - Neural mechanisms 		

Source: National Research Council (2001).

1 source-to-response conceptual framework illustrated in Figure 1-1. The NRC Committee went
2 on to delineate a series of 10 research topics that they recommended be addressed in an
3 expanded PM research program aimed at answering a set of broadly stated questions, as shown
4 in Table 1-2.

5 The EPA PM Research Program, structured to address topics shown in Table 1-2 includes,
6 for example, studies to improve understanding of the formation and composition of fine PM,
7 improved measurements and estimation of population exposures to ambient PM, the
8 characteristics or components of PM that are responsible for its health effects, factors increasing
9 susceptibility to PM effects in some subpopulations, and mechanisms by which these effects are
10 produced. The results from these efforts, and related efforts by other Federal agencies and the
11 general scientific community during the past several years, have substantially enhanced the
12 scientific and technical bases for future decisions on the PM NAAQS.

15 **1.3 CURRENT PM CRITERIA AND NAAQS REVIEW**

16 **1.3.1 Key Milestones**

17 As with other NAAQS reviews, rigorous assessment of relevant scientific information is
18 presented in this updated, revised PM AQCD. As shown in Table 1-3, development of the
19 document has involved substantial external peer review through (a) public workshops involving
20 the general aerosol scientific community, (b) iterative reviews of successive drafts by CASAC,
21 and (c) comments from the public. The final document will reflect input received through these
22 reviews and will serve to evaluate and integrate the latest available scientific information to
23 ensure that the review of the PM standards is based on rigorous evaluation of the available
24 science.

25 An earlier (October 1999) First External Review Draft of this updated document was
26 released in the fall of 1999 for public comment and CASAC review. A Second External Review
27 Draft (March 2001) took into account earlier public comments and the December 1999 CASAC
28 review and was reviewed by CASAC in July 2001. A Third External Review Draft similarly
29 took into account prior public comments and CASAC recommendations and was released in
30 early May 2002 for a 60-day public comment period; CASAC reviewed it at a public meeting in
31 July 2002.

**TABLE 1-2. RESEARCH TOPICS AND QUESTIONS RECOMMENDED BY
NATIONAL RESEARCH COUNCIL (NRC) TO BE ADDRESSED BY EXPANDED
PM RESEARCH PROGRAM**

RESEARCH TOPIC 1.	OUTDOOR MEASURES VERSUS ACTUAL HUMAN EXPOSURES
	<i>• What are the quantitative relationships between concentrations of particulate matter and gaseous co-pollutants measured at stationary outdoor air monitoring sites and the contributions of these concentrations to actual personal exposures, especially for subpopulations and individuals?</i>
RESEARCH TOPIC 2.	EXPOSURES OF SUSCEPTIBLE SUBPOPULATIONS TO TOXIC PARTICULATE MATTER COMPONENTS
	<i>• What are the exposures to biologically important constituents and specific characteristics of particulate matter that cause responses in potentially susceptible subpopulations and the general population?</i>
RESEARCH TOPIC 3.	CHARACTERIZATION OF EMISSION SOURCES
	<i>• What are the size distribution, chemical composition, and mass-emission rates of particulate matter emitted from the collection of primary-particle sources in the United States, and what are the emissions of reactive gases that lead to secondary particle formation through atmospheric chemical reactions?</i>
RESEARCH TOPIC 4.	AIR-QUALITY MODEL DEVELOPMENT AND TESTING
	<i>• What are the linkages between emission sources and ambient concentrations of the biologically important components of particulate matter?</i>
RESEARCH TOPIC 5.	ASSESSMENT OF HAZARDOUS PARTICULATE MATTER COMPONENTS
	<i>• What is the role of physicochemical characteristics of particulate matter in eliciting adverse health effects?</i>
RESEARCH TOPIC 6.	DOSIMETRY: DEPOSITION AND FATE OF PARTICLES IN THE RESPIRATORY TRACT
	<i>• What are the deposition patterns and fate of particles in the respiratory tract of individuals belonging to presumed susceptible subpopulations?</i>
RESEARCH TOPIC 7.	COMBINED EFFECTS OF PARTICULATE MATTER AND GASEOUS POLLUTANTS
	<i>• How can the effects of particulate matter be disentangled from the effects of other pollutants? How can the effects of long-term exposure to particulate matter and other pollutants be better understood?</i>
RESEARCH TOPIC 8.	SUSCEPTIBLE SUBPOPULATIONS
	<i>• What subpopulations are at increased risk of adverse health outcomes from particulate matter?</i>
RESEARCH TOPIC 9.	MECHANISMS OF INJURY
	<i>• What are the underlying mechanisms (local pulmonary and systemic) that can explain the epidemiologic findings of mortality/morbidity associated with exposure to ambient particulate matter?</i>
RESEARCH TOPIC 10.	ANALYSIS AND MEASUREMENT
	<i>• To what extent does the choice of statistical methods in the analysis of data from epidemiologic studies influence estimates of health risks from exposures to particulate matter? Can existing methods be improved? What is the effect of measurement error and misclassification on estimates of the association between air pollution and health?</i>

Source: National Research Council (2001).

TABLE 1-3. SCHEDULE FOR DEVELOPMENT OF THE CURRENT REVISED PARTICULATE MATTER AIR QUALITY CRITERIA DOCUMENT (PM AQCD)

Major Milestones	Target Dates
PM NAAQS Review Plan to CASAC	October 1997
Prepare AQCD Development Plan	November 1997 to January 1998
Begin Literature Search	February 1998
Federal Register Call for Information/Sources Sought	April 1998
CASAC Meeting on AQCD Development Plan	May 1998
Prepare Workshop Drafts of Chapters	May to December 1998
Peer Review Workshop	April 1999
Prepare External Review Draft AQCD	March to September 1999
First External Review Draft	October 1999
Public Comment Period on Draft AQCD	October 1999 to January 2000
CASAC Meeting on First Draft AQCD	December 1999
Second External Review Draft	March 2001
Public Comment Period on Second Draft	April to July 2001
CASAC Meeting on Second Draft	July 2001
Third External Review Draft	April 2002
Public Comment Period on Third Draft	May to July 2002
CASAC Meeting on Third Draft	July 2002
Final PM AQCD	Oct/Nov 2002

1 Shortly after EPA released the Third External Review Draft in May 2002, the Health
2 Effects Institute (HEI) announced that researchers at Johns Hopkins University had discovered
3 problems with applications of statistical software used in a number of important studies on links
4 between ambient air particulate matter (PM) and death and disease. In response to the surfacing
5 of such statistical issues, which affected numerous PM time-series studies that used General
6 Additive Models (GAM) and were published post-1995, EPA took steps in consultation with
7 CASAC to encourage researchers to reanalyze affected studies and to submit them expeditiously

1 for peer review by a special expert panel convened by HEI. The results of reanalyses for more
2 than 30 studies of likely importance in informing U.S. standard setting decisions for ambient PM
3 have now been peer-reviewed and are included, along with commentary by the HEI expert peer-
4 review panel, in a recently released HEI Special Report (Health Effects Institute, May 2003).
5 The subject statistical issues and reanalyses results are discussed in more detail in Chapter 8 of
6 this document. After a 60-day public comment period, starting in June 2003, and CASAC
7 review of this Fourth Draft, the final version of this PM AQCD is targeted for issuance by
8 December 31, 2003.

9 After CASAC review of the First External Review Draft of this revised PM AQCD in
10 December 1999, EPA's OAQPS started to prepare the associated PM Staff Paper (SP).
11 A preliminary draft SP was made available to the public and was discussed at a July 2001
12 CASAC meeting; and additional consultations have been held via teleconference with CASAC
13 to obtain feedback on proposed approaches to be used in conducting analyses to be included in
14 the First External Review Draft of the PM SP due to be released in the summer of 2003. The
15 draft PM SP will draw on the updated findings and conclusions from this draft PM AQCD and
16 will also undergo public comment and CASAC review (now being scheduled for November,
17 2003). Ultimately drawing on information in the final version of this newly revised PM AQCD,
18 the PM SP will evaluate policy implications of the key studies and scientific findings contained
19 in the AQCD, present related staff analyses of air quality and human health risk, and identify
20 critical elements that EPA staff believes should be considered in reviewing the PM standards.
21 The PM SP is intended to bridge the gap between the scientific review in the AQCD and the
22 public health and welfare policy judgements required of the Administrator in reviewing the PM
23 NAAQS. In doing so, the PM SP will include staff conclusions and recommendations of options
24 for the Administrator's consideration.

25 Based on the final versions of the PM AQCD and the PM SP, and on the advice of
26 CASAC, the Administrator will propose decisions as to whether to retain or revise the current
27 PM NAAQS and provide opportunities for public and CASAC comments on the proposed
28 decisions. Taking into account comments on the proposed decisions, the Administrator will then
29 make final decisions on the PM NAAQS, which are now expected to be published around the
30 end of 2005.

1.3.2 Methods and Procedures for Document Preparation

The procedures for developing this revised PM AQCD build on the experience and methods derived from the most recent previous PM, Ozone, and CO AQCD preparation efforts. Briefly, the respective responsibilities for production of the present PM AQCD are as follows. An NCEA-RTP PM Team was formed and is responsible for developing and implementing the project plan for preparation of the PM AQCD, taking into account inputs from individuals in other EPA program and policy offices identified as part of the EPA PM Work Group. The resulting project plan (i.e., the PM Document Development Plan) was discussed with CASAC in May 1998 and was appropriately revised. An ongoing literature search has continued to be conducted to identify, to the extent possible, all pertinent PM literature published since early 1996. Additionally, EPA published in the Federal Register (1) a request for information asking for recently available research information on PM that may not yet be published and (2) a request for individuals with the appropriate type and level of expertise to contribute to the writing of PM AQCD materials to identify themselves (U.S. Environmental Protection Agency, 1998b). The specific authors of chapters or sections of the proposed document were selected on the basis of their expertise on the subject areas and their familiarity with the relevant literature; these include both EPA and non-EPA scientific experts. The project team defined critical issues and topics to be addressed by the authors and provided direction in order to emphasize evaluation of those studies most clearly identified as important for standard setting. It should be noted that materials contributed by non-EPA authors are incorporated and, at times, modified by EPA PM team staff to reflect internal and/or external review comments, e.g., by the public or CASAC, and that EPA is responsible for the ultimate content of the PM AQCD.

The main focus of this revised criteria document is the evaluation and interpretation of pertinent atmospheric science information, air quality data, human exposure information, and health and welfare effects information newly published since that assessed in the 1996 PM AQCD and likely to be useful in deriving criteria for U.S. EPA PM NAAQS decisions. Initial draft versions of AQCD chapters were evaluated via expert peer-review workshop discussions and/or written peer reviews that focused on the selection of pertinent studies included in the chapters, the potential need for additional information to be added to the chapters, and the quality of the summarization and interpretation of the literature. The authors of the draft chapters then revised them on the basis of workshop and/or written expert review

1 recommendations. These and other integrative summary materials were incorporated into the
2 First External Review Draft of the PM AQCD (October 1999), which underwent public
3 comment and was the subject of consultation with CASAC at a December 1999 public meeting.

4 In order to foster timely presentation and publication of newly emerging PM research
5 findings, EPA co-sponsored an Air and Waste Management Association International Speciality
6 Conference, entitled "PM 2000: Particulate Matter and Health," held in January 2000 in
7 Charleston, SC. The conference was co-sponsored in cooperation with several other government
8 agencies and/or private organizations that also fund PM research. Topics covered included new
9 research results concerning the latest advances in PM atmospheric sciences (e.g., PM formation,
10 transport, transformation), PM exposure, PM dosimetry and extrapolation modeling, PM
11 toxicology (e.g., mechanisms, laboratory animal models, human clinical responses), and PM
12 epidemiology. The main purpose of the conference was to facilitate having the latest scientific
13 information available in time for incorporation as quickly as possible into the Second External
14 Review Draft of this revised PM AQCD. Hence, arrangements were made for scientists to
15 submit written manuscripts on papers or posters presented at the PM 2000 Conference for
16 expedited peer-review by several major journals, so that decisions on acceptance for publication
17 could be made by mid-2000. The evaluations and findings set forth in the Second External
18 Review Draft (March 2001) of the revised PM AQCD included consideration of such published
19 PM 2000 papers and extensive additional information published elsewhere since the previous
20 First External Review Draft; and the Second Draft was reviewed by CASAC in July 2001.

21 Further revisions were then incorporated into the Third External Review Draft (April 2002)
22 to reflect both public comment and CASAC review of the Second Draft, as well as assessment of
23 additional extensive new information published since that addressed in the Second Draft. This
24 Fourth Draft AQCD incorporates changes made in response to earlier public comments and
25 CASAC reviews; and it includes pertinent peer-reviewed literature published or accepted for
26 publication mainly through April 2002. The final PM AQCD will include revisions made in
27 response to public comment and CASAC review of this draft document.

1.3.3 Approach

An initial step in development of this revised PM AQCD was to focus on selection of pertinent issues to include in the document as the basis for the derivation of PM NAAQS criteria. Preliminary issues were identified by the NCEA PM Team via inputs from other EPA program and policy offices, as derived from the 1996 PM AQCD and SP, their CASAC and public reviews, from the 1997 standard promulgation process, and from the 1998 PM Research Needs Document (alluded to in Section 1.2.2). Still further identification and refinement of issues resulted from NRC review and reports on PM research priorities (also discussed in Section 1.2.2 above). The CASAC review of the PM AQCD Development Plan and public comments on earlier draft AQCD materials at various stages of their development also provided important inputs regarding issue identification.

In developing draft materials for inclusion in the revised PM AQCD, detailed review of key new research was undertaken as a first step. However, instead of presenting a comprehensive review of all the literature, emphasis in this revised AQCD is placed on (1) first, the concise summary of key findings derived from previous PM criteria reviews (especially the 1996 PM AQCD) and, then, (2) evaluation of the most pertinent new key information, with greater emphasis on more interpretive assessment — an approach reflecting CASAC recommendations. To aid in the development of a more concise document than the 1996 PM AQCD, compilation of summary tables of relevant new literature published since completion of that previous document and selective text discussion of such new literature has been undertaken, with increased emphasis being placed in text discussions on interpretive evaluation and integration of key points derived from the newly summarized research results.

1.4 DOCUMENT ORGANIZATION AND CONTENT

The present draft document attempts to critically review and assess relevant scientific literature on PM published, since early 1996, including materials accepted for publication mainly through April 2002 (and thus appearing mostly during 2002). Limited coverage of some more recent studies is also included as deemed appropriate in light of its special importance. For example, information derived from the recently released HEI Special Report (Health Effects Institute, May 2003), discussed above in Section 1.3.1, is being integrated into this assessment.

1 Literature discussed in detail in the 1996 EPA PM AQCD (U.S. Environmental Protection
2 Agency, 1996a) generally is not discussed in depth in this document; rather key findings from
3 that 1996 review are summarized as appropriate. Limited treatment is included, however, for
4 some earlier studies judged to be of particular importance in the review of the PM NAAQS.
5 Key literature is mainly summarized in tables; and the text mainly attempts to integrate and
6 discuss overall interpretive points. An attempt is made to present alternative points of view
7 where scientific controversy exists.

8 Emphasis is placed in the document on studies conducted at or near PM pollutant
9 concentrations found in ambient air. However, although emphasis has been placed on studies in
10 the range of current ambient levels, studies examining effects of higher concentrations have been
11 included if they contain unique data or documentation of a previously unreported effect or
12 mechanism.

13 The present document, basically organized to assess information related to topics along the
14 same flow of issues presented in the NRC conceptual framework shown in Figure 1-1, includes
15 an Executive Summary and nine chapters presented in two volumes. Volume I contains the
16 Executive Summary, this general introduction (Chapter 1), and Chapters 2 through 5. Chapters 2
17 and 3 provide background information on physical and chemical properties of PM and related
18 compounds; sources and emissions; atmospheric transport, transformation, and fate of PM;
19 methods for the collection and measurement of PM; and U.S. ambient air PM concentrations.
20 Chapter 4 assesses PM environmental effects on vegetation and ecosystems, visibility, man-
21 made materials, and climate-related effects (including effects on atmospheric transmission of
22 solar radiation), and includes limited information on economic impacts of some welfare effects.
23 Chapter 5 discusses factors affecting exposure of the general population to ambient PM.

24 The second volume contains Chapters 6 through 9. Chapter 6 evaluates information
25 concerning dosimetry of inhaled particles in the respiratory tract. Chapter 7 assesses the
26 toxicology of specific types of PM constituents and potential mechanisms of action, based on
27 both laboratory animal studies and controlled human exposure studies. Chapter 8 discusses
28 observational, i.e., epidemiologic, studies. Lastly, Chapter 9 integrates key information on
29 exposure, dosimetry, and critical health risk issues derived from studies reviewed in the prior
30 chapters, as well as highlighting key points regarding important welfare effects associated with
31 ambient PM.

REFERENCES

- Federal Register. (1971) National primary and secondary ambient air quality standards. F. R. (April 30) 36: 8186-8201.
- Federal Register. (1987) Revisions to the national ambient air quality standards for particulate matter. F. R. (July 1) 52: 24,634-24,669.
- Federal Register. (1996) National ambient air quality standards for particulate matter; proposed rule. F. R. (December 13) 61: 65,638-65,713.
- Federal Register. (1997) National ambient air quality standards for particulate matter; final rule. F. R. (July 18) 62: 38,652-38,752.
- Health Effects Institute. (2003) Revised analyses of time-series studies of air pollution and health. Boston, MA: Health Effects Institute; special report.
- Lioy, P. J. (1990) Assessing total human exposure to contaminants: a multidisciplinary approach. *Environ. Sci. Technol.* 24: 938-945.
- National Research Council. (1983) Risk assessment in the federal government: managing the process. Washington, DC: National Academy Press. Available: <http://books.nap.edu/books/POD115/html/index.html> (3 June 2003).
- National Research Council. (1994) Science and judgment in risk assessment. Washington, DC: National Academy Press. Available: <http://www.nap.edu/books/030904894X/html/> (4 June 2003).
- National Research Council. (1998) Research priorities for airborne particulate matter. I. Immediate priorities and a long-range research portfolio. Washington, DC: National Academy Press. Available: <http://www.nap.edu/catalog/6131.html> (4 June 2003).
- National Research Council. (1999) Research priorities for airborne particulate matter. II. Evaluating research progress and updating the portfolio. Washington, DC: National Academy Press. Available: <http://www.nap.edu/books/0309066387/html/> (4 June 2003).
- National Research Council. (2001) Research priorities for airborne particulate matter. III. Early research progress. Washington, DC: National Academy Press. Available: <http://www.nap.edu/books/0309073375/html/> (4 June 2003).
- Sexton, K.; Selevan, S. G.; Wagener, D. K.; Lybarger, J. A. (1992) Estimating human exposures to environmental pollutants: availability and utility of existing databases. *Arch. Environ. Health* 47: 398-407.
- U.S. Code. (1991) Clean Air Act, §108, air quality criteria and control techniques, §109, national ambient air quality standards. U. S. C. 42: §§7408-7409.
- U.S. Court of Appeals for the District of Columbia. (1999a) American Trucking Associations, Inc. vs. U.S. Environmental Protection Agency. 175 F3d 1027 (D.C. Cir. 1999).
- U.S. Court of Appeals for the District of Columbia. (1999b) American Trucking Associations, Inc. vs. U.S. Environmental Protection Agency. 195 F.3d 4 (D.C. Cir. 1999), affirmed in part, reversed in part, and remanded..
- U.S. Court of Appeals for the District of Columbia. (2002) American Trucking Associations, Inc. vs. U.S. Environmental Protection Agency. 283 F.3d 355, 378-79 (D.C. Cir. 2002).
- U.S. District Court of Arizona. (1995) American Lung Association v. Browner. West's Federal Supplement 884 F.Supp. 345 (No. CIV 93-643 TUC ACM).
- U.S. Environmental Protection Agency. (1996a) Air quality criteria for particulate matter. Research Triangle Park, NC: National Center for Environmental Assessment-RTP Office; report nos. EPA/600/P-95/001aF-cF. 3v.
- U.S. Environmental Protection Agency. (1996b) Review of the national ambient air quality standards for particulate matter: policy assessment of scientific and technical information. OAQPS staff paper. Research Triangle Park, NC: Office of Air Quality Planning and Standards; report no. EPA/452/R-96-013. Available from: NTIS, Springfield, VA; PB97-115406REB.
- U.S. Environmental Protection Agency. (1998a) Particulate matter research needs for human health risk assessment to support future reviews of the national ambient air quality standards for particulate matter. Research Triangle Park, NC: National Center for Environmental Assessment; report no. EPA/600/R-97/132F.
- U.S. Environmental Protection Agency. (1998b) Review of national ambient air quality standards for particulate matter. *Commer. Bus. Daily*: February 19. Available: <http://cbdnet.access.gpo.gov/index.html> [1999, November 24].
- U.S. Supreme Court. (2001) *Whitman v. American Trucking Association*. 531 U.S. 457 (nos. 99-1257 and 99-1426).
- SWolff, G. T. (1996) Closure by the Clean Air Scientific Advisory Committee (CASAC) on the staff paper for particulate matter [letter to Carol M. Browner, Administrator, U.S. EPA]. Washington, DC: U.S. Environmental Protection Agency, Clean Air Scientific Advisory Committee; EPA-SAB-CASAC-LTR-96-008; June 13.

2. PHYSICS, CHEMISTRY, AND MEASUREMENT OF PARTICULATE MATTER

Chapter 3 of the 1996 EPA document Air Quality Criteria for Particulate Matter (1996 PM AQCD; U.S. Environmental Protection Agency, 1996a) contained an extensive review of the physics and chemistry of airborne particulate matter (PM). Chapter 2 of this revised version of the PM AQCD also provides background information on the physics and chemistry of atmospheric particles, information useful in aiding the understanding of subsequent chapters. Those subsequent chapters are basically organized to follow the sequence of key elements comprising the risk assessment framework described in Chapter 1 (Section 1.2.2), beginning with sources and continuing to effects as shown in Figure 1-1. Thus, this chapter provides new information useful in evaluating PM effects of PM on human health and welfare and in preparing related risk assessments used to support PM standard-setting decisions. Information important for implementation of PM standards, but not essential to the standard setting process, is not the focus in this chapter. The reader is referred to the NARSTO Fine Particle Assessment (NARSTO, 2003) for information relevant to air quality management for PM.

Unlike other criteria pollutants (O_3 , CO, SO_2 , NO_2 , and Pb), PM is not a specific chemical entity but is a mixture of particles from different sources and of different sizes, compositions, and properties. Emphasis is placed here on discussion of differences between fine and coarse particles and differences between ultrafine particles and accumulation-mode particles within fine particles.

PM is defined quantitatively by the measurement techniques employed. Therefore, it will be useful to discuss our understanding of the relationship between PM suspended in the atmosphere, PM inhaled by people, and PM measured by various sampling and analytical techniques. Chapter 4 of the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a) contained a review of the state-of-the-art of PM measurement technology. Since that time, considerable progress has been made in understanding problems in the measurement of PM mass, chemical composition, and physical parameters. There also has been progress in developing new and improved measurement techniques, especially for continuous measurements. Therefore, a more extensive survey on measurement problems and on newly

developed measurement techniques is included in Section 2.2. For more detail and older references, the reader is referred to Chapters 3 and 4 of the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a).

2.1 PHYSICS AND CHEMISTRY OF PARTICULATE MATTER

2.1.1 Basic Concepts

Atmospheric particles originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. Examples of atmospheric particles include combustion-generated particles, such as diesel soot or fly ash; photochemically produced particles, such as those found in urban haze; salt particles formed from sea spray; and soil-like particles from resuspended dust. Some particles are liquid; some are solid. Others may contain a solid core surrounded by liquid. Atmospheric particles contain inorganic ions, metallic compounds, elemental carbon, organic compounds, and crustal compounds. Some atmospheric particles are hygroscopic and contain particle-bound water. The organic fraction is especially complex, containing hundreds (probably thousands) of organic compounds. (See Appendix 3C for information on the composition of the organic fraction and the concentration of specific organic compounds.) Primary particles are emitted directly from sources; whereas secondary particles are formed from gases through chemical reactions in the atmosphere involving atmospheric oxygen (O_2) and water vapor (H_2O); reactive species such as ozone (O_3); radicals such as the hydroxyl ($\bullet OH$) and nitrate ($\bullet NO_3$) radicals; and pollutants such as sulfur dioxide (SO_2), nitrogen oxides (NO_x), and organic gases from natural and anthropogenic sources. The particle formation process includes nucleation of particles from low-vapor pressure gases emitted from sources or formed in the atmosphere by chemical reactions, condensation of low-vapor pressure gases on existing particles, and coagulation of particles. Thus, any given particle may contain PM from many sources. Because a particle from a given source is likely to be composed of a mixture of chemical components and particles from different sources may coagulate to form a new particle, atmospheric particles may be considered a mixture of mixtures.

The composition and behavior of particles are fundamentally linked with those of the surrounding gas. An aerosol may be defined as a suspension of solid or liquid particles in air. The term aerosol includes both the particles and all vapor or gas phase components of air.

1 However, the term aerosol is sometimes used to refer to the suspended particles only. In this
2 document, "particulate" is used only as an adjective, as in particulate matter.

3 A complete description of the atmospheric aerosol would include an accounting of the
4 chemical composition, morphology, and size of each particle and the relative abundance of each
5 particle type as a function of particle size (Friedlander, 1970). However, the physical and
6 chemical characteristics of particles are usually measured separately. Size distributions by
7 particle number, used to calculate surface area and volume distributions, often are determined by
8 physical means, such as electrical mobility, aerodynamic behavior, or light scattering. Chemical
9 composition usually is determined by analysis of collected samples although some species can
10 be measured in situ. The mass and average chemical composition of particles, segregated
11 according to aerodynamic diameter by cyclones or impactors, can also be determined. However,
12 recent developments in single particle analysis techniques by electron microscopy with X-ray
13 analysis of single particles (but not agglomerates) collected on a substrate or by mass
14 spectroscopy of individual suspended particles provide elemental composition of individual
15 particles by particle size and, thus, are bringing the description envisioned by Friedlander closer
16 to reality.

18 **2.1.2 Physical Properties and Processes**

19 **2.1.2.1 Definitions of Particle Diameter**

20 The diameter of a spherical particle may be determined by optical or electron microscopy,
21 by light scattering and Mie theory, by its electrical mobility, or by its aerodynamic behavior.
22 However, atmospheric particles often are not spherical. Therefore, their diameters are described
23 by an "equivalent" diameter (i.e., the diameter of a sphere that would have the same physical
24 behavior). An optical diameter is the diameter of a spherical particle, with the same refractive
25 index as the particle used to calibrate the optical particle sizer, that scatters the same amount of
26 light into the solid angle measured. Diffusion and gravitational settling are important physical
27 behaviors for particle transport, collection, and removal processes, including deposition in the
28 respiratory tract. Different equivalent diameters are used depending on which process is more
29 important. For smaller particles diffusion is more important and the Stokes diameter is often
30 used. For larger particles gravitational setting is more important and the aerodynamic diameter
31 is often used.

1 The Stokes diameter, D_p , describes particle size based on the aerodynamic drag force
2 imparted on a particle when its velocity differs from that of the surrounding fluid. For a smooth,
3 spherically shaped particle, D_p exactly equals the physical diameter of the particle. For
4 irregularly shaped particles, D_p is the diameter of an equivalent sphere that would have the same
5 aerodynamic resistance. Electrical mobility analyzers classify particles according to their
6 electrical mobility. Particles of equal Stokes diameters that carry the same electric charge will
7 have the same electrical mobility. Hence, for spherical particles, the electrical mobility diameter
8 would equal the Stokes diameter. The mobility diameter can be considered the diameter of a
9 spherical particle that would have the same electrical mobility. The particle mobility can be
10 related to the particle diffusion coefficient and Brownian diffusion velocity through the Stokes-
11 Einstein equation. Thus, the Stokes diameter is the appropriate parameter for particle behavior
12 governed by diffusion. The Stokes diameter, D_p , is used in size distributions based on light
13 scattering and mobility analysis. The Stokes diameter is independent of density.

14 The aerodynamic diameter, D_a , however, depends on particle density. It is defined as the
15 diameter of a spherical particle with an equal gravitational settling velocity but a material density
16 of 1 g/cm³. Cascade impactors separate particles based on their aerodynamic diameter and
17 aerodynamic particle sizers measure the aerodynamic diameter. Respirable, thoracic, and
18 inhalable sampling and PM_{2.5} and PM₁₀ sampling are based on particle aerodynamic diameter.
19 For particles greater than about 0.5 μ m, the aerodynamic diameter is generally the quantity of
20 interest. For smaller particles, the Stokes diameter may be more useful. Particles with the same
21 physical size and shape but different densities will have the same Stokes diameter but different
22 aerodynamic diameters.

23 Aerodynamic diameter, D_a , is related to the Stokes diameter, D_p , by:
24

$$D_a = \left(\frac{\rho C_p}{C_a} \right)^{1/2} D_p \quad (2-1)$$

25
26 where ρ is the particle density, and C_p and C_a are the Cunningham slip factors evaluated for the
27 particle diameters D_p and D_a respectively. The slip factor is a function of the ratio between
28 particle diameter and mean free path of the suspending gas (0.066 μ m for air at one atmosphere

pressure and 20 °C). C is an empirical factor that accounts for the reduction in the drag force on particles due to the “slip” of the gas molecules at the particle surface. It is important for particles less than 1 μm in diameter, for which the surrounding air cannot be modeled by a continuous fluid. For large particles ($D_p > 5 \mu\text{m}$) $C = 1$; while for smaller particles $C > 1$.

For particles with diameters greater than the mean free path, λ , the aerodynamic diameter given by equation (2-1) is approximated by:

$$D_a = (\rho)^{1/2} D_p \quad (D_p \gg \lambda) \quad (2-2)$$

This expression, which shows that aerodynamic diameter is directly proportional to the square root of the particle density, is often used for particles as small as 0.5 μm . For particles with diameters much smaller than the mean free path, the slip factor must be taken into account. In this case the aerodynamic diameter is directly proportional to the particle density,

$$D_a = (\rho) D_p \quad (D_p \ll \lambda) \quad (2-3)$$

Detailed definitions of the various sizes and their relationships are given in standard aerosol textbooks (e.g., Friedlander [2000], Reist [1984, 1993], Seinfeld and Pandis [1998], Hinds [1999], Vincent [1989, 1995], Willeke and Baron [1993], Baron and Willeke [2002], and Fuchs [1964, 1989]).

2.1.2.2 Aerosol Size Distributions

Particle size as indexed by one of the “equivalent” diameters is an important parameter in determining the properties, effects, and fate of atmospheric particles. The atmospheric deposition rates of particles and therefore their residence times in the atmosphere are a strong function of their Stokes and aerodynamic diameters. The diameter also influences deposition patterns of particles within the lung. Because light scattering is strongly dependent on the optical particle size, the amount of light scattering per unit PM mass will be dependent on the size distribution of atmospheric particles. Therefore, the effects of atmospheric particles on

1 visibility, radiative balance, and climate will be influenced by the size distribution of the
2 particles. Studies using cascade impactors or cyclones measure the particle-size distribution
3 directly in aerodynamic diameter. The diameters of atmospheric particles range from 1 nm to
4 100 μm , spanning 5 orders of magnitude. A variety of different instruments, measuring a variety
5 of equivalent diameters, are required to cover this range.

6 Older particle counting studies used optical particle counters to cover the range of 0.3 to
7 30 μm diameter. Diameters of particles below 0.5 μm were measured as mobility diameters.
8 The particle diameters used in size distribution graphs from these studies usually are given as
9 physical or Stokes diameters rather than aerodynamic diameters. In recent years, aerodynamic
10 particle sizers have been developed that give a direct measurement of the aerodynamic diameter
11 in the range of approximately 0.7 to 10 μm diameter. These instruments have been used with
12 electrical mobility analyzers that measure the mobility diameter of particles from 3 nm to
13 approximately 0.5 μm (McMurry, 2000). Unfortunately, there is no agreed-upon technique for
14 combining the various equivalent diameters. Some workers use various assumptions to combine
15 the various measurements into one presentation; others report each instrument separately.
16 Therefore, the user of size distribution data should be careful to determine exactly which
17 equivalent diameter is reported.

18 *Particle Size Distribution Functions*

19 The distribution of particles with respect to size is an important physical parameter
20 governing their behavior. Because atmospheric particles cover several orders of magnitude in
21 particle size, size distributions often are expressed in terms of the logarithm of the particle
22 diameter on the X-axis and the measured differential concentration on the Y-axis: $\Delta N/\Delta(\log D_p)$
23 = the number of particles per cm^3 of air having diameters in the size range from $\log D_p$ to $\log(D_p$
24 $+ \Delta D_p)$. Because logarithms do not have dimensions, it is necessary to think of the distribution
25 as a function of $\log(D_p/D_{p0})$, where the reference diameter $D_{p0} = 1 \mu\text{m}$ is not explicitly stated. If
26 $\Delta N/\Delta(\log D_p)$ is plotted on a linear scale, the number of particles between D_p and $D_p + \Delta D_p$ is
27 proportional to the area under the curve of $\Delta N/\Delta(\log D_p)$ versus $\log D_p$. Similar considerations
28 apply to distributions of surface, volume, and mass. When approximated by a function, the
29 distributions are usually given as $dN/d(\log D_p)$ rather than $\Delta N/\Delta(\log D_p)$.
30
31

Atmospheric Aerosol Size Distributions

In 1978, Whitby (1978) published an analysis of over 1000 particle size distributions measured at various locations in the U.S. Figure 2-1 shows the number, surface area, and volume distributions for the grand average continental size distribution. Volume, surface area, and number distributions are plotted on an arithmetic scale such that the volume, surface area, or number of particles in any specified size range is proportional to the corresponding area under the curve. These distributions show that most of the particles are quite small, below 0.1 μm ; whereas most of the particle volume (and therefore most of the mass) is found in particles $> 0.1 \mu\text{m}$. Other averaged atmospheric size distributions are shown in Figure 2-2 and 2-3 (Whitby, 1978; Whitby and Sverdrup, 1980). Figure 2-2a and b describe the number of particles as a function of particle diameter for rural, urban-influenced rural, urban, and freeway-influenced urban aerosols. For some of the same data, the particle volume distributions are shown in Figure 2-3a and b. Whitby (1978) observed that the size distributions typically had three peaks which he called "modes." The entire size distribution could be characterized well by a trimodal model consisting of three additive log-normal distributions. The mode with a peak between 5 and 30 μm diameter, formed by mechanical processes, was named the coarse particle mode; the mode with a peak between 0.15 and 0.5 μm , formed by condensation and coagulation, was called the accumulation mode; and the mode with a peak between 0.015 and 0.04 μm , whose size was influenced by nucleation as well as by condensation and coagulation, was called the transient nuclei or Aiken nuclei range, subsequently shortened to the nuclei mode. The nuclei mode could be seen in the number and surface distribution but only in special situations was it noticeable in the mass or volume distributions. The accumulation and nuclei modes taken together were called fine particles. An idealized size distribution showing modes and formation mechanisms is shown in Figure 2-4.

Whitby (1978) concluded

The distinction between "fine particles" and "coarse particles" is a fundamental one. There is now an overwhelming amount of evidence that not only are two modes in the mass or volume distribution usually observed, but that these fine and coarse modes are usually chemically quite different. The physical separation of the fine and coarse modes originates because condensation produces fine particles while mechanical processes produce mostly coarse particles . . . the dynamics of fine particle growth ordinarily operate to prevent the fine

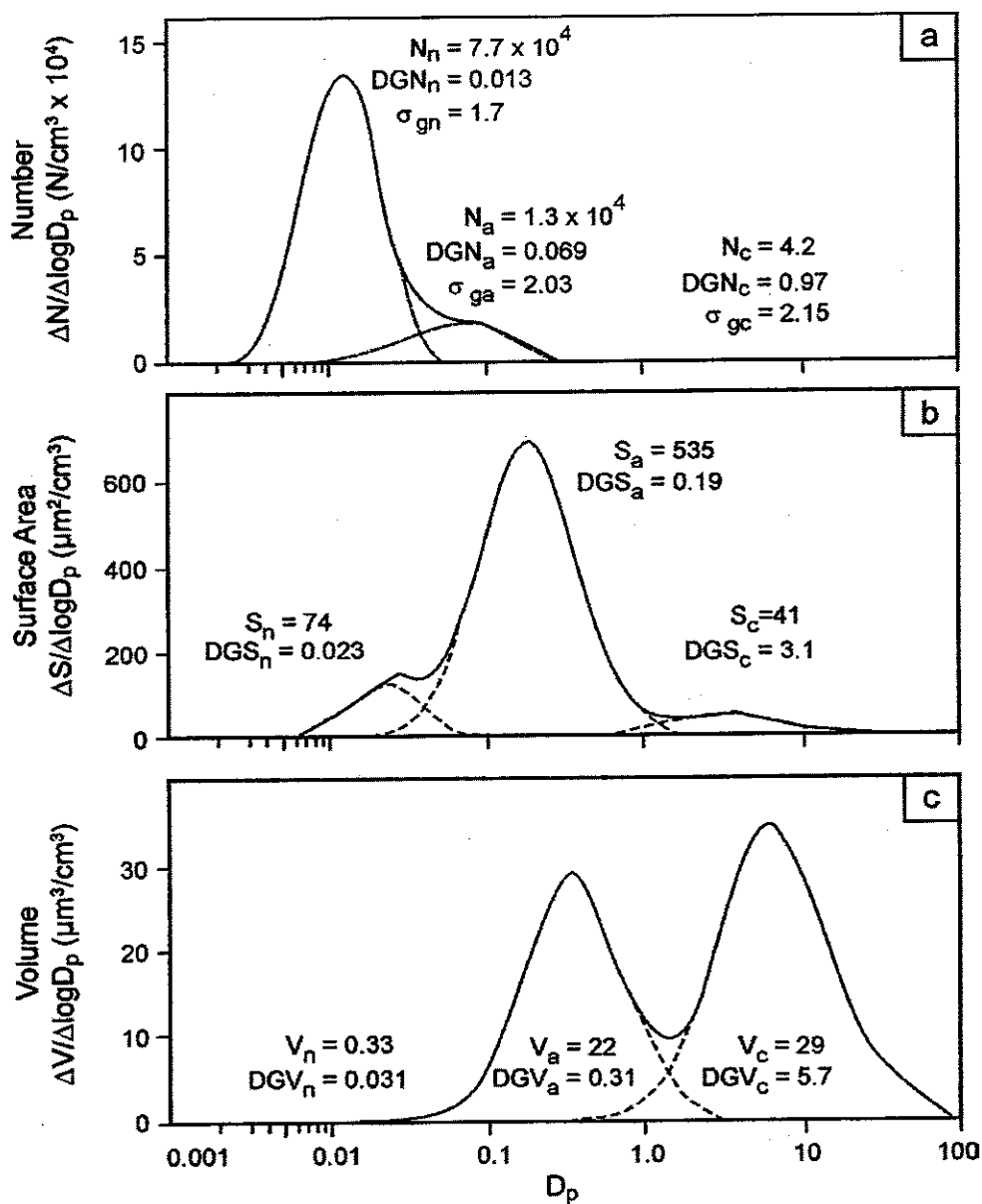


Figure 2-1. Distribution of coarse (c), accumulation (a), and nuclei (n) mode particles by three characteristics, a) number (N), b) surface area (S) and c) volume (V) for the grand average continental size distribution. DGV = geometric mean diameter by volume; DGS = geometric mean diameter by surface area; DGN = geometric mean diameter by number; D_p = particle diameter.

Source: Whitby (1978).

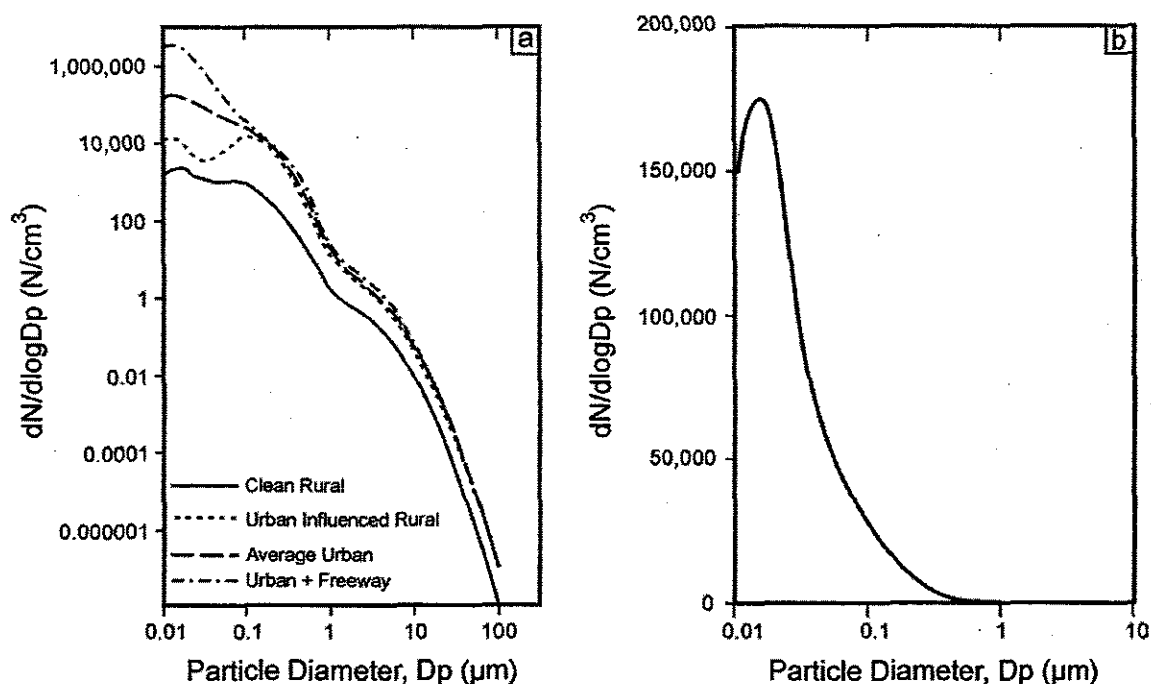


Figure 2-2. Particle size distributions by number, (a) number concentrations are shown on a logarithmic scale to display the wide range by site and size; (b) number concentrations for the average urban distribution are shown on a linear scale. For the linear scale, the area under any part of the curve is proportional to particle number in that size range.

Source: Whitby (1978); Whitby and Sverdrup (1980).

particles from growing larger than about 1 μm. Thus, the fine and coarse modes originate separately, are transformed separately, are removed separately, and are usually chemically different . . . practically all of the sulfur found in atmospheric aerosol is found in the fine particle fraction. Thus, the distinction between fine and coarse fractions is of fundamental importance to any discussion of aerosol physics, chemistry, measurement, or aerosol air quality standards.

Whitby's (1978) conclusions were based on extensive studies of size distributions in a number of western and midwestern locations during the 1970s (Whitby et al., 1974; Willeke and Whitby, 1975; Whitby, 1978; Wilson et al., 1977; Whitby and Sverdrup, 1980). No size-distribution studies of similar scope have been published since then. Newer results

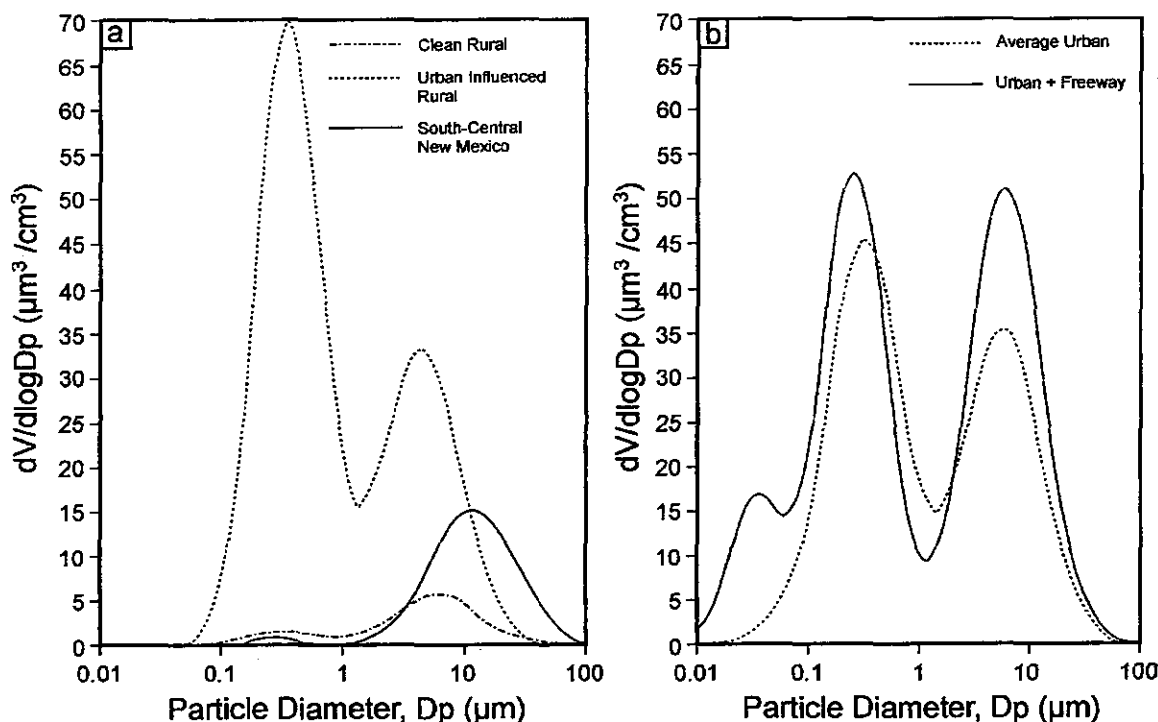


Figure 2-3. Size distribution by volume (a) for the averaged rural and urban-influenced rural number distributions shown in Figure 2-2a and a distribution from south central New Mexico, and (b) for the averaged urban and freeway-influenced urban number distributions shown in Figure 2-2a.

Source: Whitby and Sverdrup (1980); Kim et al. (1993) south central New Mexico.

from particle counting and impactor techniques, including data from Europe (U.S. Environmental Protection Agency, 1996a) and Australia (Keywood et al., 1999, 2000), show similar results for the accumulation and coarse modes. Extensive measurements of particle size distributions, as part of EPA's Supersites program, are providing much new data for analysis.

Whitby's (1978) conclusions have held up remarkably well. However, ideas about the sub-0.1 μm diameter range have changed somewhat as newer instruments provided measurements extending to smaller sizes and with greater resolution in size and time (McMurry et al., 2000). Depending on the source, temperature, saturated vapor pressure of the components, and the age of the aerosol, size distributions have been observed with peaks (including multiple peaks) throughout the sub-0.1 μm diameter size range. Sub-0.1 μm diameter peaks have been

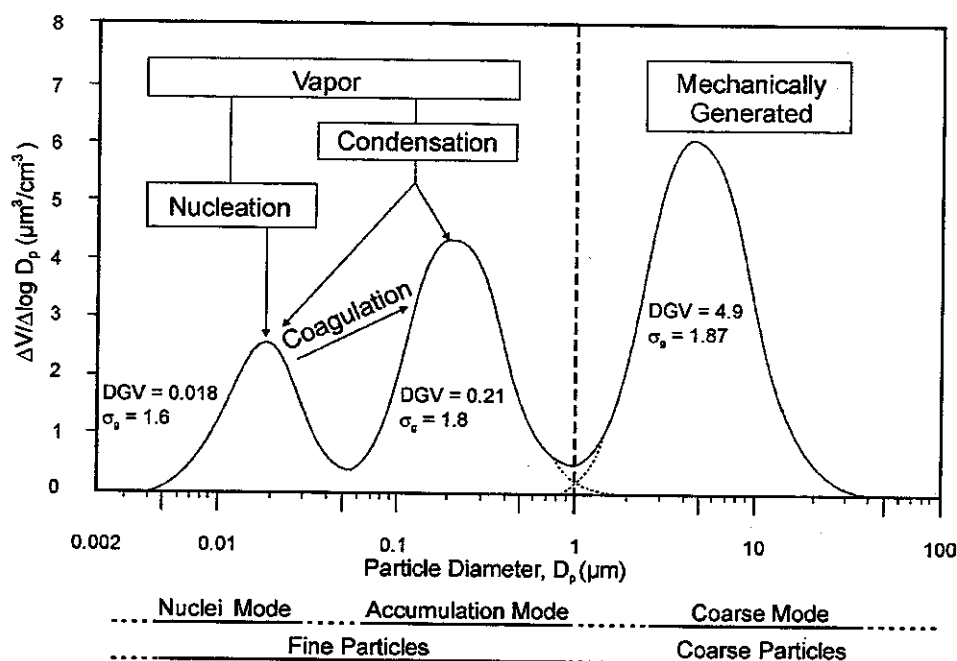


Figure 2-4. Volume size distribution, measured in traffic, showing fine and coarse particles and the nuclei and accumulation modes of fine particles. DGV (geometric mean diameter by volume, equivalent to volume median diameter) and σ_g (geometric standard deviation) are shown for each mode. Also shown are transformation and growth mechanisms (e.g., nucleation, condensation, and coagulation).

Source: Adapted from Wilson and Suh (1997).

observed in rural areas (O'Dowd, 2002) as well as for brief periods (nucleation bursts) in urban areas (Woo et al., 2001a). Based on these and other observations, discussed in detail in Section 2.1.2.3, aerosol scientists now classify particles in the sub-0.1 μm size range as ultrafine particles and divide this size range into a nucleation region ($< 10\text{ nm}$) and an Aitkin (nuclei) region (10-100 nm), as shown in Figure 2-5. Other studies, discussed in detail in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a), have shown that in fog or clouds or at very high relative humidities the accumulation mode may split into a larger size (more hygroscopic or droplet) submode and a smaller size (less hygroscopic or condensation) submode.

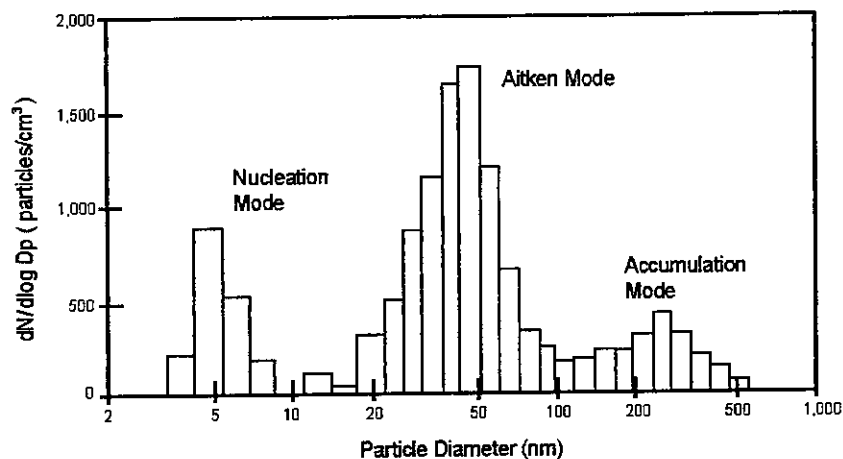


Figure 2-5. Submicron number size distribution observed in a boreal forest in Finland showing the tri-modal structure of fine particles. The total particle number concentration was 1011 particles/cm³ (10 minute average).

Source: Mäkelä et al. (1997).

1 *Definitions of Particle Size Fractions*

2 In the preceding discussion several subdivisions of the aerosol size distribution were
 3 identified. Aerosol scientists use three different approaches or conventions in the classification
 4 of particles by size: (1) modes, based on the observed size distributions and formation
 5 mechanisms; (2) cut point, usually based on the 50% cut point of the specific sampling device,
 6 including legally specified, regulatory sizes for air quality standards; and (3) dosimetry or
 7 occupational health sizes, based on the entrance into various compartments of the respiratory
 8 system.

9
 10 **Modal.** The modal classification as first proposed by Whitby (1978) is shown in
 11 Figures 2-1 and 2-4. New modes introduced since 1978 are shown in Figure 2-5. The
 12 nucleation and Aitkin modes are best observed in the number distribution. However, the Aitkin
 13 mode can be seen in the volume distribution in traffic or near traffic or other sources of ultrafine
 14 particles (Figures 2-3b and 2-4). The observed modal structure is frequently approximated by

several log-normal distributions. Definitions of terms used to describe size distributions in modal terms are given below.

Nucleation Mode: Freshly formed particles with diameters below 10 nm, observed during active nucleation events. The lower limit, where particles and large molecules overlap, is uncertain. Current techniques limit measurements to particles 3 nm or greater.

Aitkin Mode: Larger particles with diameters between 10 and 100 nm. The Aitken mode may result from growth of smaller particles or nucleation from higher concentrations of precursors. Nucleation and Aitkin nuclei modes are normally observed in the number distribution.

Accumulation Mode: Particles with diameters from about 0.1 μm to just above the minimum in the mass or volume distributions which usually occurs between 1 and 3 μm . Accumulation-mode particles normally do not grow into the coarse mode. Nucleation-mode and Aitkin-mode particles grow by coagulation (two particles combining to form one) or by condensation (low-equilibrium vapor pressure gas molecules condensing on a particle) and "accumulate" in this size range.

Coarse Mode or Coarse Particles: Particles with diameters mostly greater than the minimum in the particle mass or volume distributions, which generally occurs between 1 and 3 μm . These particles are usually formed by mechanical breakup of larger particles or bulk material.

Fine Particles: Fine particles include the nucleation, Aitkin, and accumulation modes, i.e., particles from the lowest measurable size, currently about 3 nm, to just above the minimum in the mass or volume distribution which generally occurs between 1 and 3 μm . These particles are generated during combustion or formed from gases.

Ultrafine Particles: That portion of fine particles with diameters below about 0.1 μm (100 nm), i.e., the Aitkin and nucleation modes.

1 Modes are defined primarily in terms of their formation mechanisms but also differ in
2 terms of sources, composition, age, and size. Nucleation mode applies to newly formed particles
3 which have had little chance to grow by condensation or coagulation. Aitkin mode particles are
4 also recently formed particles that are still actively undergoing coagulation. However, because
5 of higher concentrations of precursors or more time for condensation and coagulation, the
6 particles have grown to larger sizes. Accumulation mode applies to the final stage as particles,
7 originally formed as nuclei, grow to a point where growth slows down. These three modes,
8 which together are called fine particles, are formed primarily by combustion or chemical
9 reactions of gases yielding products with low saturated vapor pressures. Fine particles include
10 metals and elemental and organic carbon (primary PM) and sulfate, nitrate, ammonium ions, and
11 organic compounds (secondary PM).

12 The coarse mode refers to particles formed by mechanical breakdown of minerals, crustal
13 material, and organic debris. The composition includes primary minerals and organic material.
14 The accumulation mode and the coarse mode overlap in the region between 1 and 3 μm (and
15 occasionally over an even larger range). In this region, chemical composition of individual
16 particles can usually, but not always, allow identification of a source or formation mechanism
17 and so permit identification of a particle as belonging to the accumulation or coarse mode.

18
19 ***Sampler Cut Point.*** Another set of definitions of particle size fractions arises from
20 considerations of size-selective sampling. Size-selective sampling refers to the collection of
21 particles below or within a specified aerodynamic size range. Size fractions are usually specified
22 by the 50% cut point size; e.g., $\text{PM}_{2.5}$ refers to particles collected by a sampling device that
23 collects 50% of 2.5 μm particles and rejects 50% of 2.5 μm particles. However, size fractions
24 are defined, not merely by the 50% cut point, but by the entire penetration curve. Examples of
25 penetration curves are given in Figure 2-6. Thus, as shown by Figure 2-6, a $\text{PM}_{2.5}$ sampler, as
26 defined by the Federal Reference Method, rejects 94% of 3 μm particles, 50% of 2.5 μm
27 particles, and 16% of 2 μm . Samplers with the same 50% cut point but differently shaped
28 penetration curves would collect different fractions of PM. Size-selective sampling has arisen in
29 an effort to measure particle size fractions with some special significance (e.g., health, visibility,
30 source apportionment, etc.), to measure mass size distributions, or to collect size-segregated
31 particles for chemical analysis. Dichotomous samplers split the particles into smaller and larger

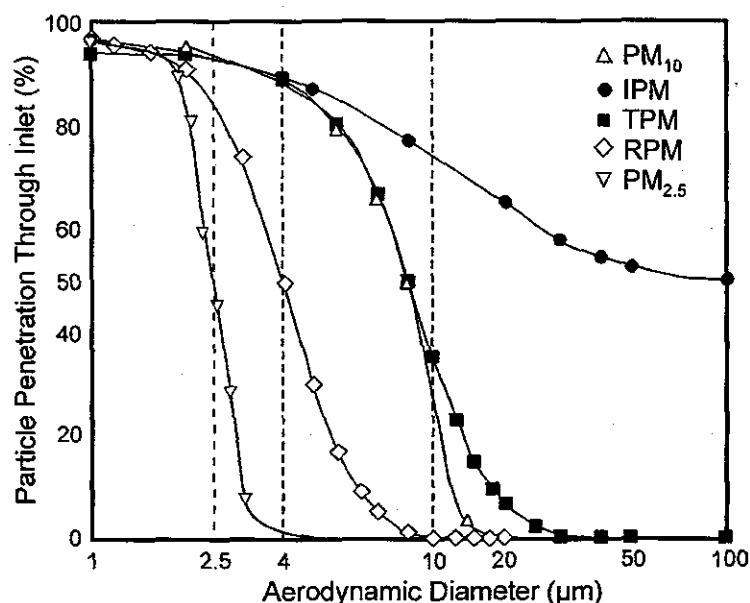


Figure 2-6. Specified particle penetration (size-cut curves) through an ideal (no-particle-loss) inlet for five different size-selective sampling criteria. Regulatory size cuts are defined in the Code of Federal Regulations; PM_{2.5} (2001c), PM₁₀ (2001a). PM_{2.5} is also defined in the Federal Register (1997). Size-cut curves for inhalable particulate matter (IPM), thoracic particulate matter (TPM) and respirable particulate matter (RPM) size cuts are computed from definitions given by American Conference of Governmental and Industrial Hygienists (1994).

fractions that may be collected on separate filters. However, some fine particles ($\approx 10\%$) are collected with the coarse particle fraction. Cascade impactors use multiple size cuts to obtain a distribution of size cuts for mass or chemical composition measurements. One-filter samplers with a variety of upper size cuts are also used, e.g., PM_{2.5}, PM₁₀.

Regulatory size cuts are a specific example of size-selective sampling. In 1987, the NAAQS for PM were revised to use PM₁₀, rather than total suspended particulate matter (TSP), as the indicator for the NAAQS for PM (Federal Register, 1987). The use of PM₁₀ as an indicator is an example of size-selective sampling based on a regulatory size cut (Federal Register, 1987). The selection of PM₁₀ as an indicator was based on health considerations and was intended to focus regulatory concern on those particles small enough to enter the thoracic region of the human respiratory tract. The PM_{2.5} standard set in 1997 is also an example of

size-selective sampling based on a regulatory size cut (Federal Register, 1997). The $PM_{2.5}$ standard was based primarily on epidemiologic studies using concentrations measured with $PM_{2.5}$ samplers as an exposure index. However, the $PM_{2.5}$ sampler was not designed to collect all respirable particles; it was designed to collect fine particles because of their different sources and properties (Whitby et al., 1974). Thus, the need to attain a $PM_{2.5}$ standard will tend to focus regulatory concern on control of sources of fine particles.

Prior to 1987, the indicator for the NAAQS for PM was TSP. TSP is defined by the design of the High Volume Sampler (hivol) that collects all of the fine particles but only part of the coarse particles (Figure 2-7). The upper cut-off size of the hivol depends on the wind speed and direction and may vary from 25 to 40 μm . The Wide Range Aerosol Classifier (WRAC) was designed specifically to collect the entire coarse mode using an impaction system designed by Lundgren to collect particles up to 100 μm in diameter (Lundgren and Burton, 1995).

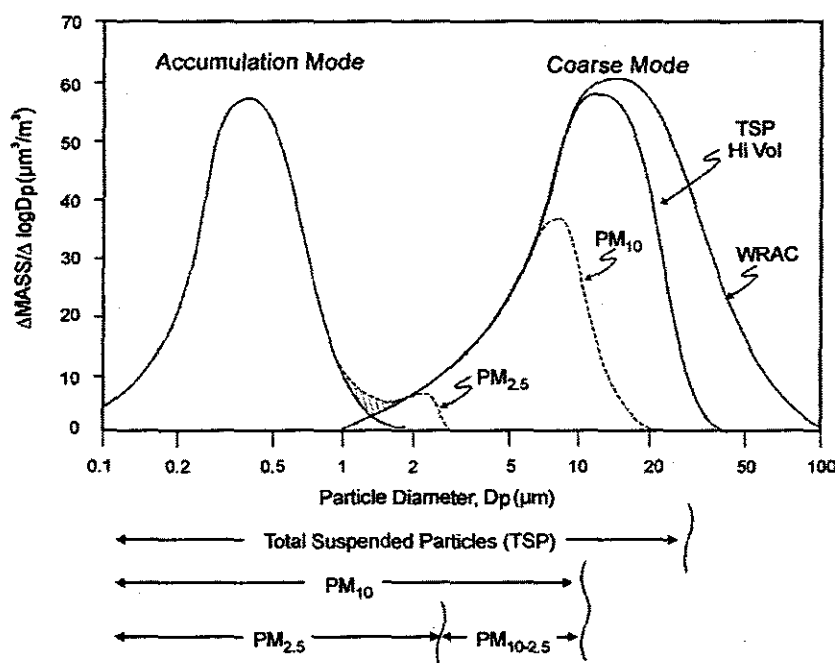


Figure 2-7. An idealized distribution of ambient particulate matter showing fine-mode particles and coarse-mode particles and the fractions collected by size-selective samplers. (WRAC is the Wide Range Aerosol Classifier which collects the entire coarse mode [Lundgren and Burton, 1995].)

Source: Adapted from Wilson and Suh (1997) and Whitby (1978).

1 An idealized distribution with the normally observed division of ambient aerosols into
2 fine-mode particles and coarse-mode particles and the size fractions collected by the WRAC,
3 TSP, PM₁₀, PM_{2.5} and PM_{10-2.5} samplers is shown in Figure 2-7. PM₁₀ samplers, as defined in
4 Appendix J to Title 40 Code of Federal Regulations (40 CFR) Part 50 (Code of Federal
5 Regulations, 2001a; Federal Register, 1987), collect all of the fine-mode particles and part of the
6 coarse-mode particles. The upper cut point is defined as having a 50% collection efficiency at
7 10 ± 0.5 μ m aerodynamic diameter. The slope of the collection efficiency curve is defined in
8 amendments to 40 CFR, Part 53, (Code of Federal Regulations, 2001b). An example of a PM₁₀
9 size-cut curve is shown in Figure 2-6.

10 An example of a PM_{2.5} size-cut curve is also shown in Figure 2-6. The PM_{2.5} size-cut
11 curve, however, is defined by the design of the Federal Reference Method (FRM) Sampler. The
12 basic design of the FRM sampler is given in the Federal Register (1997, 1998) and as 40 CFR
13 Part 50, Appendix L (Code of Federal Regulations, 2001c). Additional performance
14 specifications are given in 40 CFR Parts 53 and 58 (Code of Federal Regulations, 2001b,d).
15 In order to be used for measurement of PM_{2.5} to determine compliance with the PM_{2.5} NAAQS,
16 each specific sampler design and its associated manual of operational procedures must be
17 designated as a reference method under 40 CFR Part 53 in Section 1.2 of Appendix L (Code of
18 Federal Regulations, 2001c). Thus PM_{2.5} FRM samplers may have somewhat different designs
19 (see Table 2-4 in Section 2.2.4.1.2).

20 Papers discussing PM₁₀ or PM_{2.5} frequently insert an explanation such as "PM_x (particles
21 less than x μ m diameter)" or "PM_x (nominally, particles with aerodynamic diameter \leq x μ m)."
22 While these explanations may seem easier than "PM_x, (particles collected with an upper 50% cut
23 point of x μ m aerodynamic diameter and a specified penetration curve)," they are not entirely
24 correct and may be misleading since they suggest an upper 100% cut point of x μ m. Some
25 countries use PM₁₀ to refer not to samplers with a 50% cut at 10 μ m D_a but to samplers with
26 100% rejection of all particles greater than 10 μ m D_a. Such samplers miss a fraction of coarse
27 thoracic PM. An example is shown in Figure 2-8.

28 PM₁₀, as defined by EPA, refers to particles collected by a sampler with an upper 50% cut
29 point of 10 μ m D_a and a specific, fairly sharp, penetration curve. PM_{2.5} is analogously defined.
30 Although there is not yet an FRM, PM_{10-2.5} refers either to particles collected by a sampler with
31 an upper 50% cut point of 10 μ m D_a and a lower 50% cut point of 2.5 μ m D_a or to the difference

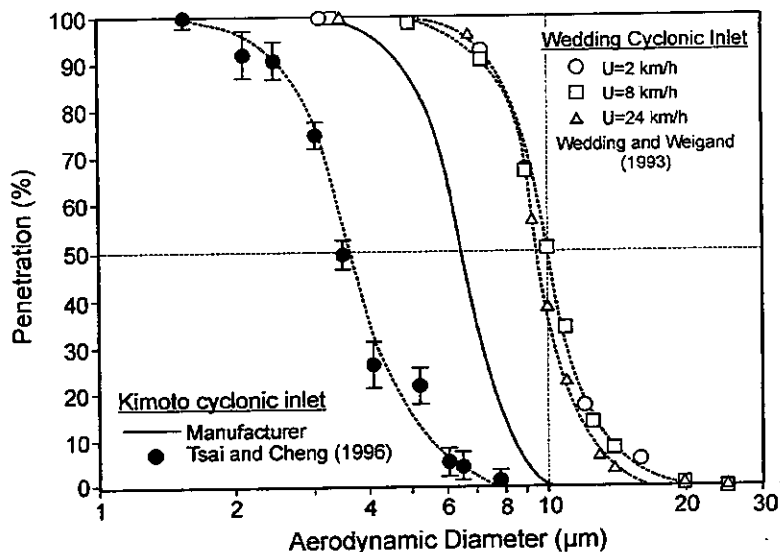


Figure 2-8. Comparison of penetration curves for two PM_{10} beta gauge samplers using cyclone inlets. The Wedding PM_{10} sampler uses the U.S. EPA definition of PM_x as $x = 50\%$ cut point. The Kimoto PM_{10} defines PM_x as $x =$ the 100% cut point (or zero penetration).

Source: Tsai and Cheng (1996).

between the particle concentration measured by a PM_{10} monitor and a $PM_{2.5}$ monitor. In all cases, the fraction of PM collected depends on the entire penetration curve (or curves); i.e., for $PM_{2.5}$ some particles $> 2.5 \mu m D_a$ are collected and not all particles $< 2.5 \mu m D_a$ are collected.

In an analysis reported in 1979, EPA scientists endorsed the need to measure fine and coarse particles separately (Miller et al., 1979). Based on the availability of a dichotomous sampler with a separation size of $2.5 \mu m D_a$, they recommended $2.5 \mu m D_a$ as the cut point between fine and coarse particles. Because of the wide use of this cut point, the $PM_{2.5}$ fraction is frequently referred to as “fine” particles. However, although the $PM_{2.5}$ sample will usually contain all of the fine particles, it may collect a small fraction of the coarse particles, especially in dry areas or during dry conditions. A $PM_{10-2.5}$ size fraction may be obtained from a dichotomous sampler or by subtracting the mass collected by a $PM_{2.5}$ sampler from the mass collected by a PM_{10} sampler. The resulting $PM_{10-2.5}$ mass, or $PM_{10-2.5}$, is sometimes called “coarse” particles. However, it would be more correct to call $PM_{2.5}$ an indicator of fine particles

(because it contains some coarse particles) and $PM_{10-2.5}$ an indicator of the thoracic component of coarse particles (because it excludes some coarse particles below $2.5 \mu m D_a$ and above $10 \mu m D_a$). It would be appropriate to call PM_{10} an indicator of thoracic particles. PM_{10} and thoracic PM, as shown in Figure 2-6, have the same 50% cut point. However, the thoracic cut is not as sharp as the PM_{10} cut; therefore, thoracic PM contains some particles between 10 and $30 \mu m$ diameter that are excluded from PM_{10} .

Over the years, the terms fine and coarse, as applied to particles, have lost the precise meaning given in Whitby's (1978) definition. In any given article, therefore, the meaning of fine and coarse, unless defined, must be inferred from the author's usage. In this document, fine particles means all particles in the nucleation, Aitken, and accumulation modes; and coarse particles means all particles in the coarse mode. $PM_{2.5}$ and fine particles are not equivalent terms.

Occupational Health or Dosimetric Size Cuts. The occupational health community has defined size fractions in terms of their entrance into various compartments of the respiratory system. This convention classifies particles into inhalable, thoracic, and respirable particles according to their upper size cuts. Inhalable particles enter the respiratory tract, including the head airways. Thoracic particles travel past the larynx and reach the lung airways and the gas-exchange regions of the lung. Respirable particles are a subset of thoracic particles that are more likely to reach the gas-exchange region of the lung. In the past, exact definitions of these terms have varied among organizations. As of 1993, a unified set of definitions was adopted by the American Conference of Governmental Industrial Hygienists (ACGIH, 1994), the International Standards Organization (ISO), and the European Standardization Committee (CEN). The curves which define inhalable (IPM), thoracic (TPM), and respirable (RPM) particulate matter are shown in Figure 2-6. These curves should not be taken to indicate that particles $> 4 \mu m D_a$ do not reach the gas exchange regions or that particles $< 4 \mu m D_a$ do not deposit in the bronchi. See Figure 6-13 for a graphical characterization of particle deposition in regions of the respiratory system as a function of particle size.

2.1.2.3 Ultrafine Particles

As discussed in Chapter 7 (Toxicology of Particulate Matter in Humans and Laboratory Animals) and in Chapter 8 (Epidemiology of Human Health Effects Associated with Ambient Particulate Matter), some scientists argue that ultrafine particles may pose potential health problems and that some health effects may be associated with particle number or particle surface area as well as or more closely than with particle mass. Some additional attention will be given to ultrafine particles because they contribute the major portion of particle number and a significant portion of particle surface area.

Formation and Growth of Fine Particles

Several processes influence the formation and growth of particles. New particles may be formed by nucleation from gas phase material. Particles may grow by condensation as gas phase material condenses on existing particles; and particles also may grow by coagulation as two particles combine to form one. Gas phase material condenses preferentially on smaller particles, and the rate constant for coagulation of two particles decreases as the particle size increases. Therefore, ultrafine particles grow into the accumulation mode; but accumulation-mode particles do not normally grow into the coarse mode (see Figure 2-4). More information and references on formation and growth of fine particles can be found in the 1996 AQCD PM (U.S. Environmental Protection Agency, 1996a).

Equilibrium Vapor Pressures

An important parameter in particle nucleation and in particle growth by condensation is the saturation ratio, S , defined as the ratio of the partial pressure of a species, p , to its equilibrium vapor pressure above a flat surface at a specified temperature, p_o : $S = p/p_o$. For either condensation or nucleation to occur, the species vapor pressure must exceed its equilibrium vapor pressure. For particles, the equilibrium vapor pressure is not the same as p_o . Two effects are important: (1) the Kelvin effect, which is an increase in the equilibrium vapor pressure above the surface due to its curvature (very small particles have higher vapor pressures and will not be stable to evaporation until they attain a critical size) and (2) the solute effect, which is a decrease in the equilibrium vapor pressure of the liquid due to the presence of other compounds in solution. Organic compounds may also be adsorbed on ultrafine carbonaceous particles.

1 For an aqueous solution of a nonvolatile salt, the presence of the salt decreases the
2 equilibrium vapor pressure of the water over the droplet. This effect is in the opposite direction
3 of the Kelvin effect, which increases the equilibrium vapor pressure above a droplet because of
4 its curvature. The existence of an aqueous solution will also influence the vapor pressure of
5 water-soluble species. The vapor pressure behavior of mixtures of several liquids or of liquids
6 containing several solutes is complex.

7 8 ***New Particle Formation***

9 When the vapor concentration of a species exceeds its equilibrium concentration
10 (expressed as its equilibrium vapor pressure), it is considered condensable. Condensable species
11 can either condense on the surface of existing particles or can nucleate to form new particles.
12 The relative importance of nucleation versus condensation depends on the rate of formation of
13 the condensable species and on the surface or cross-sectional area of existing particles (McMurry
14 and Friedlander, 1979). In ambient urban environments, the available particle surface area is
15 usually sufficient to rapidly scavenge the newly formed condensable species. Formation of new,
16 ultrafine particles is usually not observable in mass or volume distributions except near sources
17 of condensable species. Wilson et al. (1977) report observations of the Aitkin nuclei mode in
18 traffic. However, bursts of new particle formation can be observed in urban areas in the number
19 distribution (Woo et al., 2001a; McMurray et al., 2000). New particle formation also can be
20 observed in cleaner, remote regions. Bursts of new particle formation in the atmosphere under
21 clean conditions usually occur when aerosol surface area concentrations are low (Covert et al.,
22 1992). High concentrations of nuclei mode particles have been observed in regions with low
23 particle mass concentrations indicating that new particle formation is inversely related to the
24 available aerosol surface area (Clarke, 1992).

25 26 ***Sources of Ultrafine Particles***

27 Ultrafine particles are the result of nucleation of gas phase species to form condensed
28 phase species with very low equilibrium vapor pressure. In the atmosphere there are four major
29 classes of substances that yield particulate matter with equilibrium vapor pressures low enough
30 to form nuclei mode particles:

- (1) *Particles containing heavy metals.* Nuclei mode particles of metal oxides or other metal compounds are generated when metallic impurities in coal or oil are vaporized during combustion and the vapor undergoes nucleation. Metallic ultrafine particles also may be formed from metals in lubricating oil or fuel additives that are vaporized during combustion of gasoline or diesel fuels. Ultrafine metallic particles were discussed in Section 6.9 of the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a).
- (2) *Elemental carbon or soot (EC).* EC particles are formed primarily by condensation of C_2 molecules generated during the combustion process. Because EC has a very low equilibrium vapor pressure, ultrafine EC particles can nucleate even at high temperatures (Kittelson, 1998; Morawska et al., 1998).
- (3) *Organic carbon (OC).* Recent smog chamber studies and indoor experiments show that atmospheric oxidation of certain organic compounds found in the atmosphere can produce highly oxidized organic compounds with an equilibrium vapor pressure sufficiently low to result in nucleation (Kamens et al., 1999; Weschler and Shields, 1999).
- (4) *Sulfates.* Sulfuric acid (H_2SO_4) molecules are generated in the atmosphere by conversion of sulfur dioxide (SO_2) to H_2SO_4 . As H_2SO_4 is formed, it can either nucleate to form new ultrafine particles, or it can condense on existing ultrafine or accumulation mode particles (Clark and Whitby, 1975; Whitby, 1978). Nucleation theory allows calculation of nucleation rates for both binary nucleation, involving water and sulfuric acid (Easter and Peters, 1994) or ternary nucleation, which requires sulfuric acid, ammonia (NH_3), and water (Korhonen et al., 1999). Kulmala et al. (2000) compared nucleation rates of binary and ternary nucleation and concluded that the ternary rate is 1,000 times the binary rate. Results from an aerosol dynamics model with a ternary nucleation scheme indicate that nucleation in the troposphere should be ubiquitous and yield a reservoir of thermodynamically stable sulfate clusters 1-3 nm in diameter. The growth of these clusters to a detectable size (> 3 nm diameter) is limited by the availability of condensable vapor. Observations of atmospheric particle formation and growth from a continental and a coastal site suggest that a growth process including ternary nucleation is

responsible for the formation of cloud condensation nuclei. Nucleation processes in the atmosphere may also involve organic compounds as well as sulfuric acid, ammonia, and water. However, current formulations of nucleation theory only include the three inorganic components. (The possible formation of ultrafine NH_4NO_3 by reaction of NH_3 and nitric acid (HNO_3) vapor has not been investigated.)

Vehicle engine exhaust may include all these substances. Ultrafine particles are observed in the emissions from spark, diesel, and jet engines (Kittelson, 1998). In these cases it seems likely that elemental carbon, organic compounds, ammonia and sulfuric acid from sulfur in the fuel, as well as metal additives in the fuel or fuel oil, may contribute to the formation of ultrafine particles (Tobias et al., 2001). An example of particles from a diesel engine showing number and volume distributions is given in Figure 2-9.

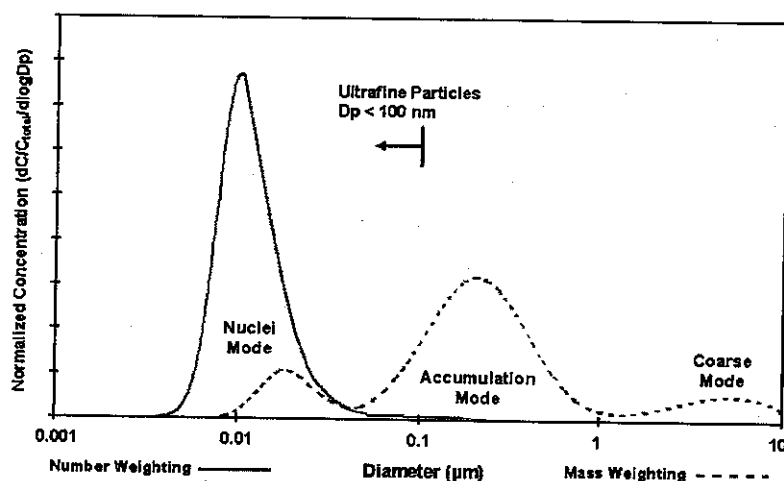


Figure 2-9. Typical engine exhaust size distribution.

Source: Kittelson (1998).

Recent Measurements of Ultrafine Particles

Instruments, developed during the past decade, permit measurement of size distributions down to 3 nm diameter particles. Use of these techniques have led to new information on the formation of new particles by nucleation. Such measurements have been carried out during intensive field measurement campaigns, during continuous measurements in urban areas in several European cities, and in the U.S. as a part of the Supersite program (McMurry et al., 2000; Woo et al., 2001a). Nucleation has been observed in the free troposphere (Weber et al., 1999; Clarke, 1992; Schröder and Ström, 1997; Raes et al., 1997); in outflows of evaporating convective clouds (Clarke et al., 1998; Hegg et al., 1990, 1991; Radke and Hobbs, 1991; Perry and Hobbs, 1994); in the marine boundary layer (Covert et al., 1992; Hoppel et al., 1994; Van Dingenen et al., 1995; Weber et al., 1998; Clarke et al., 1998); downwind of coastal regions during low tide (McGovern et al., 1996; McGovern, 1999); on mountains (Weber et al., 1995, 1997; Raes et al., 1997; Wiedensohler et al., 1997); over forests (Mäkelä et al., 1997; Kulmala et al., 1998; O'Dowd et al., 2002); downwind of certain biogenic emissions (Weber et al., 1998); in urban areas (Birmili and Wiedensohler, 1998; McMurry et al., 2000; Woo et al., 2001a); near freeways (Zhu et al., 2002a,b); in engine exhaust (Kittelson, 1998; Tobias et al., 2001); and in homes (Wallace and Howard-Reed, 2002). Nucleation events in outdoor air almost always occur during daylight, indicating that photochemistry plays a role in producing the gas phase precursors of new particles.

The number size distributions observed over a boreal forest in Finland before and during the initial stages of a nucleation event are shown in Figure 2-10. The Aitken and accumulation modes can be seen clearly before the nucleation event. The nucleation mode, with a peak between 3 and 7 nm, appears during the event. Figure 2-11 shows the variety of size distributions that may be observed as nuclei are formed and grow, based on size distributions measured in the Arctic marine boundary layer (Covert et al., 1996). These distributions all show a trimodal distribution within the fine particle size range. The changes in size distribution due to coagulation (and dilution) immediately downwind of a freeway (Zhu et al., 2002b) are shown in Figure 2-12(a)-(g). At 30 m downwind the nucleation mode is larger than the Aitken mode, but by 60 m downwind coagulation has removed particles from the nucleation mode and added particles to the Aitken mode so that the Aitken mode is larger than the nucleation mode.

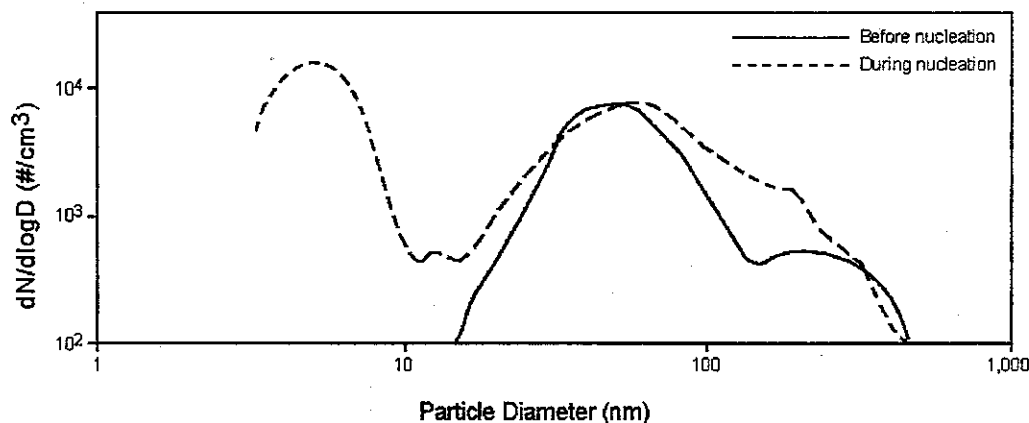


Figure 2-10. Number size distributions showing measurement of a nucleation burst made in a boreal forest in Finland.

Source: O'Dowd et al. (2002).

There is strong evidence that sulfuric acid vapor often participates in nucleation. However, condensation of sulfuric acid and its associated water and ammonium ions typically can account for only 10% to 20% of the observed growth rates for freshly nucleated particles. Therefore, organic compounds may account for much of the formation and growth of freshly nucleated particles. Evidence of nucleation of organic particles comes from smog chamber studies (Kamens et al., 1999) and from field studies over forests (Mäkelä et al., 1997; Kulmala et al., 1998; O'Dowd et al., 2002). Nucleation of organic particles may also occur indoors due to the reaction of infiltrated ozone with indoor terpenes from air fresheners or cleaning solutions (Weschler and Shields, 1999). The observation of bursts of nuclei-mode particles in Atlanta (Woo et al., 2001a), perhaps due to unusually high rates of production of condensable species, suggests that high concentrations of ultrafine particles may be a normal occurrence in polluted urban areas.

Concentration of Ultrafine Particles: A Balance Between Formation and Removal

Nuclei-mode particles may be removed by dry deposition or by growth into the accumulation mode. This growth takes place as other low vapor pressure material condenses on the particles or as nuclei-mode particles coagulate with themselves or with accumulation mode

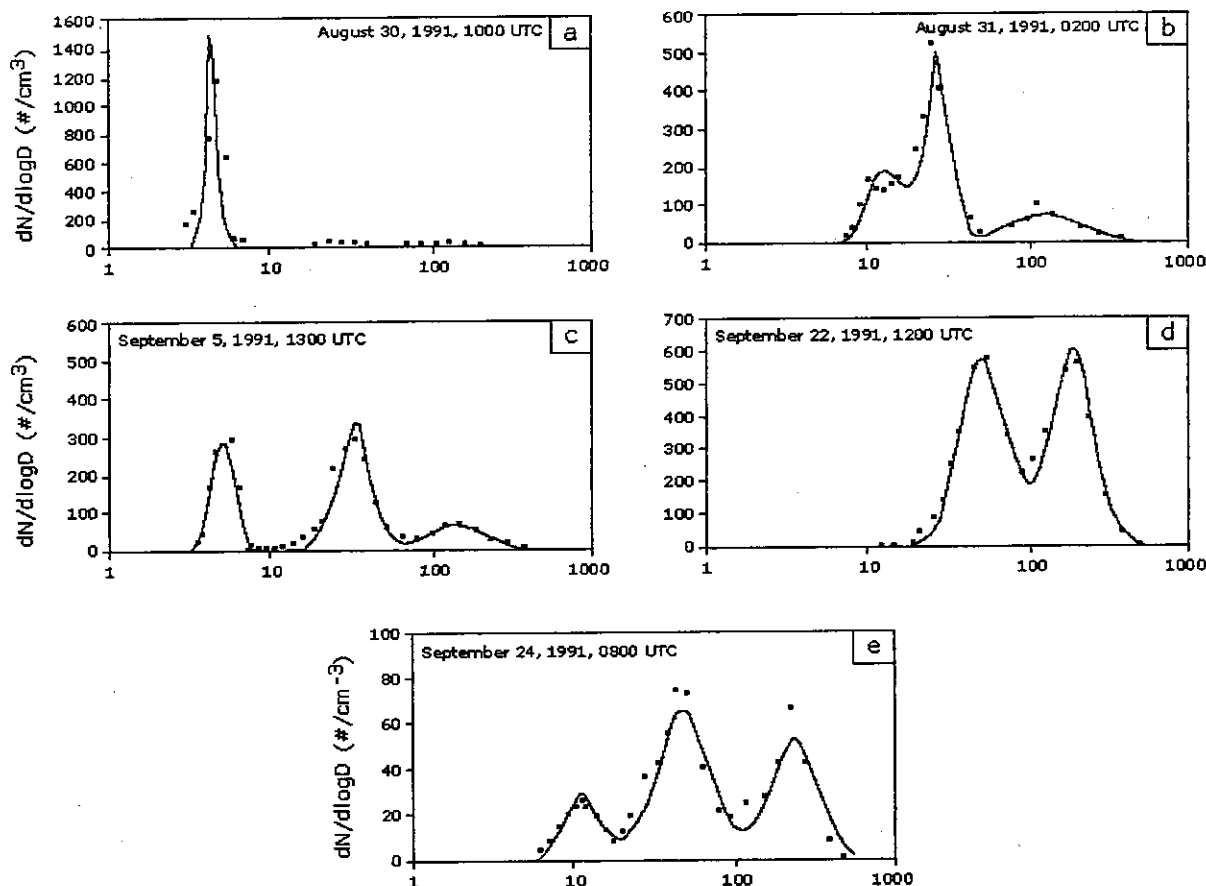


Figure 2-11. Examples of the measured one hour average particle number size distributions and the log normal fits to the modes of the data. Squares are measured data, solid lines are the fitted log normal modes determined by DistFit™. These modes, nucleation between 3 and 20 nm, Aitken between 20 and 100 nm, and accumulation above 100 nm can be observed in most examples.

Source: Covert et al. (1996).

1 particles. Because the rate of coagulation would vary with the concentration of accumulation-
 2 mode particles, it might be expected that the concentration of nuclei-mode particles would
 3 increase with a decrease in accumulation-mode mass. On the other hand, the concentration of
 4 particles would be expected to decrease with a decrease in the rate of generation of particles by
 5 reduction in emissions of metal and carbon particles or a decrease in the rate of generation of
 6 H_2SO_4 or condensable organic vapor. The rate of generation of H_2SO_4 depends on the

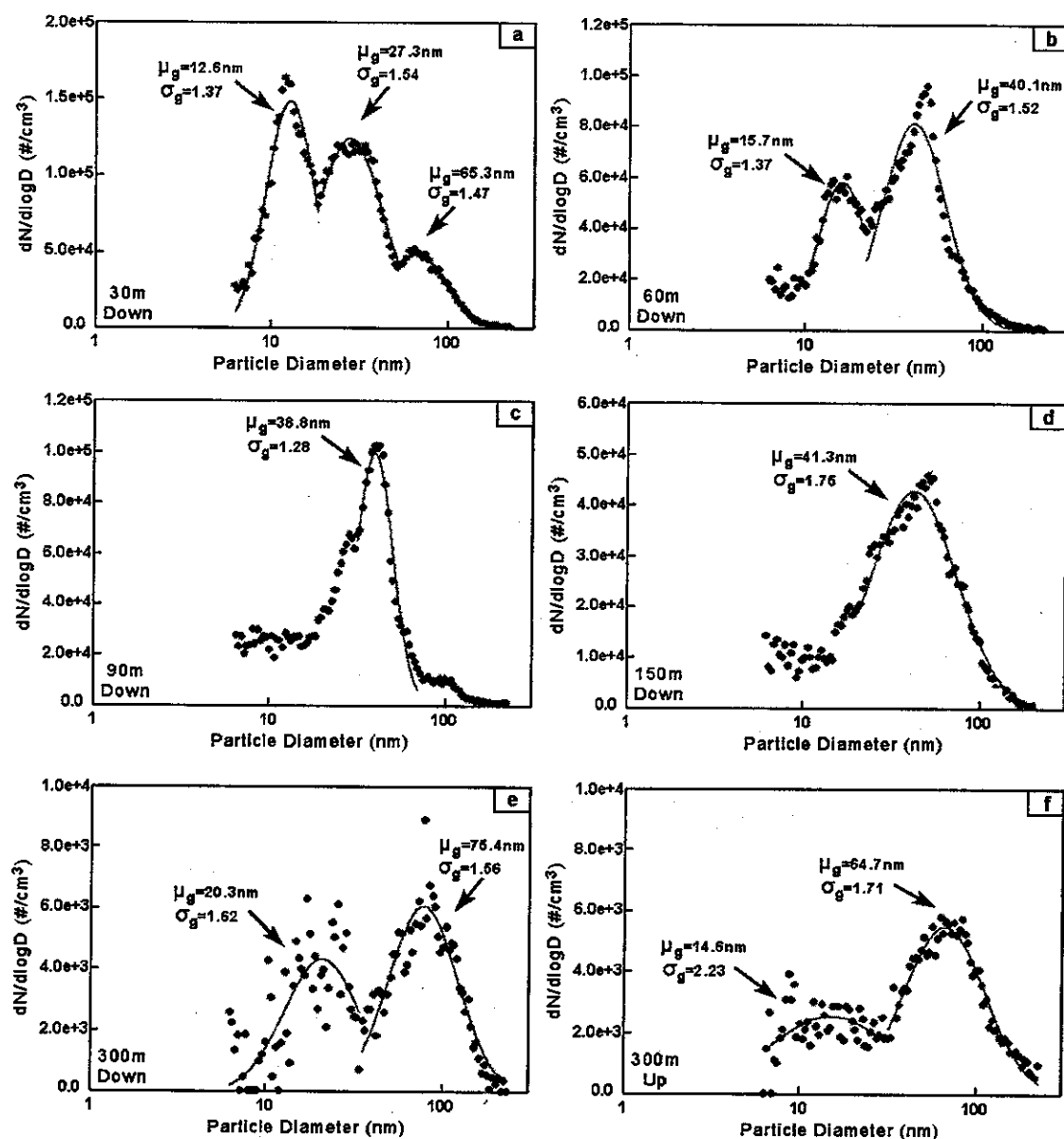


Figure 2-12(a-f). Fitted multi-model particle size distribution at different sampling distances from freeway 405 (a) 30 m downwind, (b) 60 m downwind, (c) 90 m downwind, (d) 150 m downwind, (e) 300 m downwind, (f) 300 m upwind. Size distributions were normalized to the control CPC's reading. Note different scales for $dN/d \log D_p$ axis. Modal parameters given are: geometric mean diameter, μ_g ; and geometric standard deviation, σ_g .

Source: Zhu et al. (2002b).

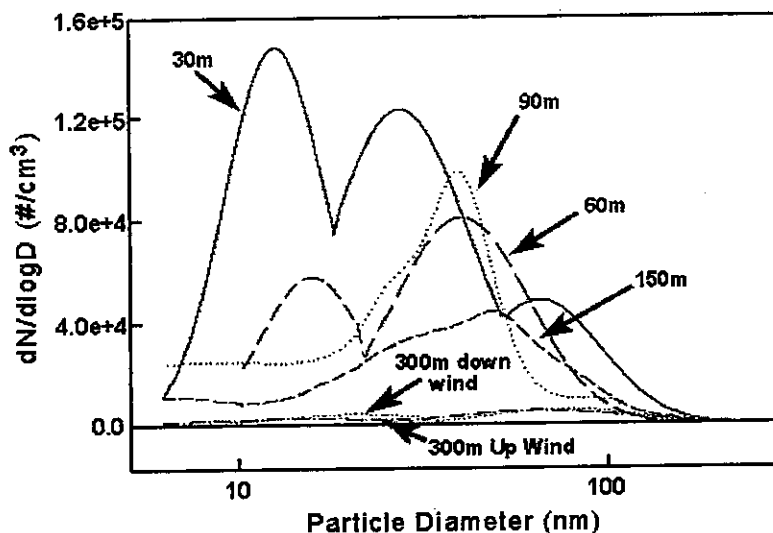


Figure 2-12(g). (Combination of a-e with $dN/d \log D_p$ scale.) Ultrafine particle size distribution at different sampling locations near the 405 freeway in Los Angeles, CA.

Source: Zhu et al. (2002b).

concentration of SO_2 and hydroxyl radical ($\bullet OH$), which is generated primarily by reactions involving ozone (O_3). Thus, reductions in SO_2 and O_3 would lead to a decrease in the rate of generation of H_2SO_4 and condensable organic vapor and to a decrease in the concentration of nuclei-mode particles. The balance between formation and removal is uncertain. However, these processes can be modeled using a general dynamic equation for particle size distribution (Friedlander, 2000) or by aerosol dynamics modules in newer air quality models (Binkowski and Shanker, 1995; Binkowski and Ching, 1995).

2.1.3 Chemistry of Atmospheric Particulate Matter

The major constituents of atmospheric PM are sulfate, nitrate, ammonium, and hydrogen ions; particle-bound water; elemental carbon; a great variety of organic compounds; and crustal material. Atmospheric PM also contains a large number of elements in various compounds and concentrations. More information and references on the composition of PM measured in a large number of studies in the United States, may be found in 1996 PM AQCD (U.S. Environmental

Protection Agency, 1996a). In this document, the composition and concentrations of PM are discussed in Chapter 3, Section 3.1, Patterns and Trends in Ambient PM_{2.5} Concentrations and ambient data for concentrations and composition of PM_{2.5} are given in Appendices 3A, 3B, and 3C.

2.1.3.1 Chemical Composition and Its Dependence on Particle Size

Studies conducted in most parts of the United States indicate that sulfate, ammonium, and hydrogen ions; elemental carbon, secondary organic compounds and primary organic species from cooking and combustion; and certain transition metals are found predominantly in the fine particle mode. Crustal materials such as calcium, aluminum, silicon, magnesium, and iron are found predominately in the coarse particles. Some primary organic materials such as pollen, spores, and plant and animal debris are also found predominantly in the coarse mode. Some components such as potassium and nitrate may be found in both the fine and coarse particle modes but from different sources or mechanisms. Potassium in coarse particles comes from soil. Potassium also is found in fine particles in emissions from burning wood or cooking meat. Nitrate in fine particles comes primarily from the reaction of gas-phase nitric acid with gas-phase ammonia to form particulate ammonium nitrate. Nitrate in coarse particles comes primarily from the reaction of gas-phase nitric acid with preexisting coarse particles.

2.1.3.2 Primary and Secondary Particulate Matter

Particulate material can be primary or secondary. PM is called "primary" if it is in the same chemical form in which it was emitted into the atmosphere. PM is called "secondary" if it is formed by chemical reactions in the atmosphere. Primary coarse particles are usually formed by mechanical processes. This includes material emitted in particulate form such as wind-blown dust, sea salt, road dust, and combustion-generated particles such as fly ash and soot. Primary fine particles are emitted from sources either directly as particles or as vapors that rapidly condense to form ultrafine or nuclei-mode particles. This includes soot from diesel engines, a great variety of organic compounds condensed from incomplete combustion or cooking, and compounds of As, Se, Zn, etc., that condense from vapor formed during combustion or smelting. The concentration of primary particles depends on their emission rate, transport and dispersion, and removal rate from the atmosphere.

1 Secondary PM is formed by chemical reactions of free, adsorbed, or dissolved gases. Most
2 secondary fine PM is formed from condensable vapors generated by chemical reactions of
3 gas-phase precursors. Secondary formation processes can result in either the formation of new
4 particles or the addition of particulate material to pre-existing particles. Most of the sulfate and
5 nitrate and a portion of the organic compounds in atmospheric particles are formed by chemical
6 reactions in the atmosphere. Secondary aerosol formation depends on numerous factors
7 including the concentrations of precursors; the concentrations of other gaseous reactive species
8 such as ozone, hydroxyl radical, peroxy radicals, or hydrogen peroxide; atmospheric conditions
9 including solar radiation and relative humidity (RH); and the interactions of precursors and
10 pre-existing particles within cloud or fog droplets or in the liquid film on solid particles. As a
11 result, it is considerably more difficult to relate ambient concentrations of secondary species to
12 sources of precursor emissions than it is to identify the sources of primary particles.
13 A significant effort is currently being directed toward the identification and modeling of organic
14 products of photochemical smog including the conversion of gases to particulate matter. More
15 information of the transformation of precursor gases into secondary PM is given in Chapter 3,
16 Section 3.3.1, Chemistry of Secondary PM Formation.

17 Particle strong acidity is due almost entirely to H_2SO_4 or NH_4HSO_4 . Thus, the acidity of
18 atmospheric particles depends on both the amount of SO_2 that is oxidized to SO_3 and
19 subsequently forms H_2SO_4 and the amount of ammonia available to react with the sulfuric acid.
20 Nitric acid is more volatile than sulfuric acid. Thus, if gas phase SO_3 or sulfuric acid or particles
21 containing H_2SO_4 or NH_4HSO_4 contact particles containing NH_4NO_3 , nitric acid gas will be
22 released with the remaining ammonia contributing to further neutralization of the acid. Little
23 NH_4NO_3 is found in atmospheres containing significant particle strong acidity. However, as SO_2
24 emissions are reduced to the point that there is more than enough ammonia to neutralize the
25 sulfuric acid, NH_4NO_3 particles will begin to form. Thus, ammonia emissions and
26 concentrations relative to those of SO_2 and H_2SO_4 are important in determining the strong acidity
27 in the atmosphere and the concentration of particulate NH_4NO_3 . Therefore, once SO_2 emissions
28 have been reduced to the point that ammonia and sulfate are in balance to form $(\text{NH}_4)_2\text{SO}_4$,
29 further reductions in SO_2 will not result in an equivalent reduction in airborne PM because one
30 $(\text{NH}_4)_2\text{SO}_4$ unit will be replaced by two NH_4NO_3 units.

2.1.3.3 Particle-Vapor Partitioning

Several atmospheric aerosol species, such as ammonium nitrate and certain organic compounds, are semivolatile and are found in both gas and particle phases. A variety of thermodynamic models have been developed to predict the temperature and relative humidity dependence of the ammonium nitrate equilibria with gaseous nitric acid and ammonia. However, under some atmospheric conditions, such as cool, cold, or very clean air, the relative concentrations of the gas and solid phases are not accurately predicted by equilibrium considerations alone, and transport kinetics can be important. The gas-particle distribution of semivolatile organic compounds depends on the equilibrium vapor pressure of the compound, total particle surface area, particle composition, atmospheric temperature, and relative humidity. Although it generally is assumed that the gas-particle partitioning of semivolatile organics is in equilibrium in the atmosphere, neither the equilibria nor the kinetics of redistribution are well understood. Diurnal temperature fluctuations cause gas-particle partitioning to be dynamic on a time scale of a few hours and can cause semivolatile compounds to evaporate during the sampling process. The pressure drop across the filter can also contribute to the loss of semivolatile compounds. The dynamic changes in gas-particle partitioning caused by changes in temperature, pressure, and gas-phase concentration, both in the atmosphere and after collection, cause serious sampling problems that are discussed in Section 2.2.3, Measurement of Semivolatile Particulate Matter.

Equilibria with Water Vapor

As a result of the equilibrium of water vapor with liquid water in hygroscopic particles, many ambient particles contain liquid water (particle-bound water). Unless removed, this particle-bound water will be measured as a component of the particle mass. Particle-bound water is important in that it influences the size of the particles, and in turn, their light scattering properties and their aerodynamic properties, which are important for deposition to surfaces, to airways following inhalation, and in sampling instrumentation. The aqueous solution provides a medium for reactions of dissolved gases including reactions that do not take place in the gas phase. The aqueous solutions also may act as a carrier to convey soluble toxic species to the gas-exchange regions of the respiratory system, including species that would be removed by deposition in the upper airways if the particles had remained in the gas phase (Friedlander and

1 Yeh, 1998; Kao and Friedlander, 1995; Wilson, 1995). An extensive review of equilibrium with
2 water vapor as it pertains to ambient aerosols was given in Chapter 3 of the 1996 PM AQCD
3 (U.S. Environmental Protection, Agency, 1996a).

4 The interaction of particles with water vapor may be described briefly as follows.
5 As relative humidity increases, particles of crystalline soluble salts, such as $(\text{NH}_4)_2\text{SO}_4$,
6 NH_4HSO_4 , or NH_4NO_3 , undergo a phase transition to become aqueous solution particles.
7 According to the phase rule, for particles consisting of a single component, this phase transition
8 is abrupt, taking place at a relative humidity that corresponds to the vapor pressure of water
9 above the saturated solution (the deliquescence point). With a further increase in relative
10 humidity, the solution particle adds water (and the concentration of the solute decreases) so that
11 the vapor pressure of the solution is maintained equal to that of the surrounding relative
12 humidity; thus, the solution particle tends to follow the equilibrium growth curve. As relative
13 humidity decreases, the solution particle follows the equilibrium curve to the deliquescence
14 point. However, rather than crystallizing at the deliquescence relative humidity, the solute
15 remains dissolved in a supersaturated solution to considerably lower relative humidities.
16 Ultimately the solution particle abruptly loses its water vapor (efflorescence) and typically
17 returns to the initial crystalline form.

18 For particles consisting of more than one component, the solid to liquid transition will take
19 place over a range of relative humidities with an abrupt onset at the lowest deliquescence point
20 of the several components and with subsequent growth as crystalline material in the particle
21 dissolves according to the phase diagram for the particular multicomponent system. Under such
22 circumstances, a single particle may undergo several more or less abrupt phase transitions until
23 the soluble material is fully dissolved. At decreasing relative humidity, such particles tend to
24 remain in solution to relative humidities well below the several deliquescence points. In the case
25 of the sulfuric acid-ammonium sulfate-water system, the phase diagram is fairly well
26 understood. For particles of composition intermediate between NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$, this
27 transition occurs in the range from 40% to below 10%, indicating that for certain compositions
28 the solution cannot be dried in the atmosphere. At low relative humidities, particles of this
29 composition would likely be present in the atmosphere as supersaturated solution droplets (liquid
30 particles) rather than as solid particles. Thus, they would exhibit hygroscopic rather than
31 deliquescent behavior during relative humidity cycles.

1 Other pure compounds, such as sulfuric acid, are hygroscopic (i.e., they form aqueous
2 solutions at any relative humidity and maintain a solution vapor pressure over the entire range of
3 relative humidity). Soluble organic compounds may also contribute to the hygroscopicity of the
4 atmospheric aerosol (Saxena et al., 1995; Saxena and Hildeman, 1996), but the equilibria
5 involving organic compounds and water vapor, and, especially for mixtures of salts, organic
6 compounds, and water, are not so well understood. These equilibrium processes may cause an
7 ambient particle to significantly increase its diameter at relative humidities above about 40%
8 (Figure 2-13). A particle can grow to five times its dry diameter as the RH approaches 100%
9 (Figure 2-14). The Federal Reference Methods, for filter measurements of PM_{2.5} and PM₁₀ mass,
10 require equilibration at a specified, low relative humidity after collection (for PM_{2.5}, between
11 30 and 40% RH with control of $\pm 5\%$ RH [Code of Federal Regulations, 2001a]). This
12 equilibration removes much of the particle-bound water and provides a relatively stable PM
13 mass for gravimetric measurements (see Section 2.2 for details and references). Otherwise,
14 particle mass would be a function of relative humidity, and the particle mass would be largely
15 particle-bound water at higher relative humidities. However, some particle-bound water may be
16 retained even after equilibration. Recent studies have shown that significant amounts of particle-
17 bound water are retained in particles collected on impaction surfaces even after equilibration and
18 that the amount of retained particle-bound water increases with relative humidity during
19 collection (Hitzenberger et al., 1997).

20 The retention of particle-bound water is a greater problem for continuous monitors that
21 measure changes in mass collected on a filter over long sampling times. If particle-bound water
22 is not removed, changes in relative humidity would cause changes in the mass of PM collected
23 over previous hours or days. These changes could be much greater than amount of PM mass
24 added in one hour. Therefore, continuous monitoring techniques generally attempt to remove
25 particle-bound water before measurement either by heating or dehumidification. However, other
26 semivolatile materials (e.g., ammonium nitrate and organic compounds) that may be partially
27 lost during sampling or equilibration of an unheated filter are certainly lost when the collected
28 sample is heated above ambient temperature. These changes in particle size with relative
29 humidity also mean that particle measurements such as surface area or volume, or composition
30 as a function of size, should be made at the same RH in order for the results are to be
31

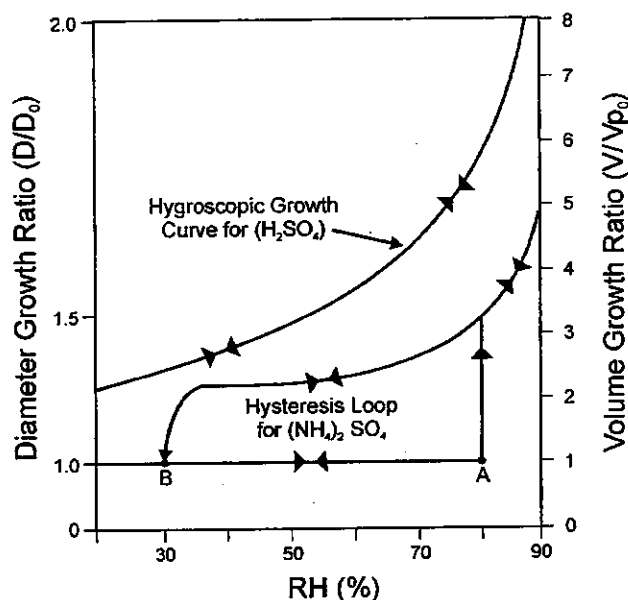


Figure 2-13. Particle growth curves showing fully reversible hygroscopic growth of sulfuric acid (H_2SO_4) particles, deliquescent growth of ammonium sulfate $[(\text{NH}_4)_2 \text{SO}_4]$ particles at the deliquescent point (A, about 80% relative humidity [RH]), reversible hygroscopic growth of ammonium sulfate solution droplets at RH greater than 80%, and hysteresis (the droplet remains supersaturated as the RH decreases below 80%) until the crystallization point (B, about 38% RH) is reached (adapted from National Research Council, 1993 and Tang, 1980).

Source: National Research Council (1993) adapted from Tang (1980).

comparable. These problems are addressed in more detail in Section 2.2, Measurement of Particulate Matter.

2.1.3.4 Atmospheric Lifetimes and Removal Processes

The lifetimes of particles vary with size. Nuclei-mode particles rapidly grow into the accumulation mode. However, the accumulation mode does not grow into the coarse mode. Accumulation-mode fine particles are kept suspended by normal air motions and have very low deposition rates to surfaces. They can be transported thousands of km and remain in the atmosphere for a number of days. Coarse particles can settle rapidly from the atmosphere within

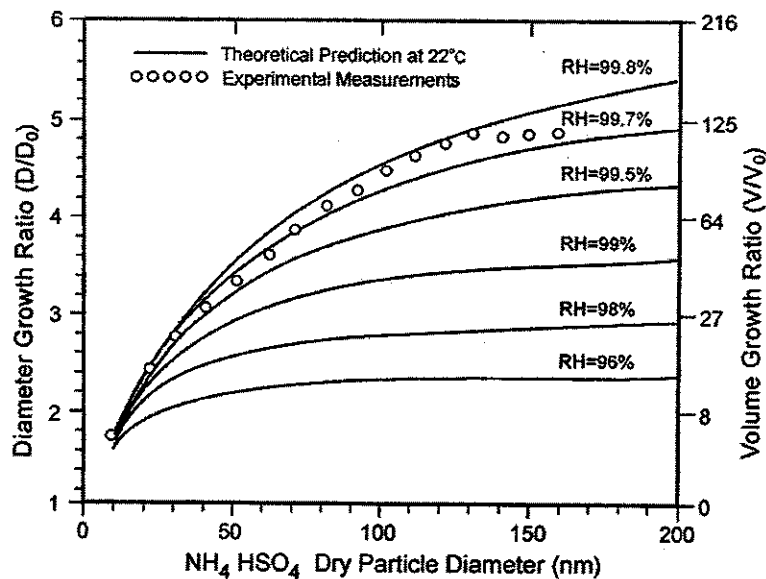


Figure 2-14. Theoretical predictions and experimental measurements of growth of NH_4HSO_4 particles at relative humidity between 95 and 100%.

Source: Li et al. (1992).

hours and normally travel only short distances. However, when mixed high into the atmosphere, as in dust storms, the smaller-sized coarse-mode particles have longer lives and travel greater distances. Dry deposition rates are expressed in terms of a deposition velocity that varies with particle size, reaching a minimum between 0.1 and 1.0 μm aerodynamic diameter (e.g., Lin et al., 1994). Accumulation-mode particles are removed from the atmosphere primarily by cloud processes. Fine particles, especially particles with a hygroscopic component, grow as the relative humidity increases, serve as cloud condensation nuclei, and grow into cloud droplets. If the cloud droplets grow large enough to form rain, the particles are removed in the rain. Falling rain drops impact coarse particles and remove them. Ultrafine or nuclei-mode particles are small enough to diffuse to the falling drop, be captured, and be removed in rain. Falling rain drops, however, are not nearly as effective in removing accumulation-mode particles as the cloud processes mentioned above. A more detailed discussion of particle deposition, including acid deposition, especially as it applies to deposition to vegetation, soil, and water surfaces is given in Chapter 4 (Environmental Effects of Airborne Particulate Matter). Acid deposition and

1 PM are intimately related, first, because particles contribute to the acidification of rain and,
2 secondly, because the gas-phase species that lead to dry deposition of acidity are also precursors
3 of particles. Therefore, reductions in SO₂ and NO_x emissions will decrease both acidic
4 deposition and PM concentrations.

5 Sulfate, nitrate, and some partially oxidized organic compounds are hygroscopic and act as
6 nuclei for the formation of cloud droplets. These droplets serve as chemical reactors in which
7 (even slightly) soluble gases can dissolve and react. Thus, SO₂ can dissolve in cloud droplets
8 and be oxidized to sulfuric acid by dissolved ozone or hydrogen peroxide. These reactions take
9 place only in aqueous solution, not in the gas phase. Sulfur dioxide also may be oxidized by
10 dissolved oxygen. This process will be faster if metal catalysts such as iron or manganese are
11 present in solution. If the droplets evaporate, larger particles are left behind. If the droplets
12 grow large enough, they will fall as rain; and the particles will be removed from the atmosphere
13 with potential effects on the materials, plants, or soil on which the rain falls. (Similar
14 considerations apply to dew.) Atmospheric particles that nucleate cloud droplets also may
15 contain other soluble or nonsoluble materials such as metal salts and organic compounds that
16 may add to the toxicity of the rain. Sulfuric acid, ammonium nitrate, ammonium sulfates, and
17 organic particles also are deposited on surfaces by dry deposition. The utilization of ammonium
18 by plants leads to the production of acidity. Therefore, dry deposition of particles can also
19 contribute to the ecological impacts of acid deposition. These effects are discussed in Chapter 4
20 (Environmental Effects of Airborne Particulate Matter).

21 22 **2.1.4 Comparison of Fine and Coarse Particles**

23 The physical and chemical properties of fine particles (including ultrafine particles and
24 accumulation-mode particles) and coarse particles are summarized for comparison purposes in
25 Table 2-1. These include important differences in sources, formation mechanisms, composition,,
26 atmospheric residence time, removal processes, and travel distances. Ensuing chapters in this
27 document will also show that fine and coarse particles differ in aspects of concentrations,
28 exposure, dosimetry, toxicology, and epidemiology. Collectively, these differences continue to
29 warrant consideration of fine particles as a separate air pollutant class from coarse particles and
30 the setting of separate standards for fine and coarse particles.

**TABLE 2-1. COMPARISON OF AMBIENT PARTICLES,
FINE PARTICLES (Ultrafine Plus Accumulation-Mode) AND COARSE PARTICLES**

	Fine		
	Ultrafine	Accumulation	Coarse
Formation Processes:	Combustion, high-temperature processes, and atmospheric reactions		Break-up of large solids/droplets
Formed by:	Nucleation Condensation Coagulation	Condensation Coagulation Reactions of gases in or on particles Reactions of gases in or on particles Evaporation of fog and cloud droplets in which gases have dissolved and reacted	Mechanical disruption (crushing, grinding, abrasion of surfaces) Evaporation of sprays Suspension of dusts Reactions of gases in or on particles
Composed of:	Sulfate Elemental Carbon Metal compounds Organic compounds with very low saturation vapor pressure at ambient temperature	Sulfate, Nitrate, Ammonium, and Hydrogen ions Elemental carbon Large variety of organic compounds Metals: compounds of Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, etc. Particle-bound water	Suspended soil or street dust Fly ash from uncontrolled combustion of coal, oil, and wood Nitrates/chlorides from HNO ₃ /HCl Oxides of crustal elements (Si, Al, Ti, Fe) CaCO ₃ , NaCl, sea salt Pollen, mold, fungal spores Plant and animal fragments Tire, brake pad, and road wear debris
Solubility:	Probably less soluble than accumulation mode	Largely soluble, hygroscopic, and deliquescent	Largely insoluble and nonhygroscopic
Sources:	Combustion Atmospheric transformation of SO ₂ and some organic compounds High temperature processes	Combustion of coal, oil, gasoline, diesel fuel, wood Atmospheric transformation products of NO _x , SO ₂ , and organic compounds, including biogenic organic species (e.g., terpenes) High-temperature processes, smelters, steel mills, etc.	Resuspension of industrial dust and soil tracked onto roads and streets Suspension from disturbed soil (e.g., farming, mining, unpaved roads) Construction and demolition Uncontrolled coal and oil combustion Ocean spray Biological sources
Atmospheric half-life:	Minutes to hours	Days to weeks	Minutes to hours
Removal Processes:	Grows into accumulation mode Diffuses to raindrops	Forms cloud droplets and rains out Dry deposition	Dry deposition by fallout Scavenging by falling rain drops
Travel distance:	<1 to 10s of km	100s to 1000s of km	<1 to 10s of km (100s to 1000s in dust storms)

Source: Adapted from Wilson and Suh (1997).

2.2 MEASUREMENT OF PARTICULATE MATTER

The 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a) summarized sampling and analytical techniques for PM and acid deposition that had appeared in the literature since the earlier 1982 PM AQCD (U.S. Environmental Protection Agency, 1982). Excellent reviews have also been published by Chow (1995) and McMurry (2000). This section discusses problems in measuring PM; new techniques that attempt to alleviate these problems or measure problem species; Federal Reference Methods, speciation monitors, analytical methods for inorganic elements, organic and elemental carbon, and ionic species; and continuous and multiday monitors.

2.2.1 Particle Measurements of Interest

There are many PM components and parameters that are of interest across the various types of uses to which PM measurement data are applied. These uses include analyses of compliance with air quality standards and trends; source category apportionment studies related to the develop of pollution reduction strategies and the validation of air quality models; studies related to health, ecological, and radiative effects; and characterization of current air quality for presentation to the public in the context of EPA's Air Quality Index. PM measurement components and parameters of specific interest for these various purposes are noted below and summarized in Table 2-2.

Particle measurements are needed to determine if a location is in compliance with air quality standards, to determine long-term trends in air quality patterns, and for epidemiologic studies. For these purposes, precision of the measurements by a variety of measurement instruments in use is a critical consideration. Therefore, intercomparisons of various samplers under a variety of atmospheric and air quality conditions are important.

In order to reduce pollution to attain a standard, pollution control agencies and national research organizations need measurements to identify source categories and to develop and validate air quality models. For these purposes, PM parameters other than mass, such as chemical composition and size distribution, must also be measured. Moreover, measurements are needed with shorter time resolution in order to match changes in pollution with diurnal changes in the boundary layer.

**TABLE 2-2. PARTICULATE MATTER COMPONENTS/PARAMETERS OF
INTEREST FOR HEALTH, ECOLOGICAL, OR RADIATIVE EFFECTS;
FOR SOURCE CATEGORY APPORTIONMENT STUDIES;
OR FOR AIR QUALITY MODELING EVALUATION STUDIES**

-
- Particle number
 - Particle surface area
 - Particle size distribution
 - PM mass (fine PM mass [PM_{2.5}] and coarse thoracic PM mass [PM_{10-2.5}]) including both nonvolatile mass as measured by the current Federal Reference method and total mass (including semivolatile components such as ammonium nitrate and semivolatile organic compounds, but not particle-bound water)
 - Ions (sulfate, nitrate, and ammonium)
 - Strong acidity (H⁺)
 - Elemental carbon
 - Organic carbon (total, nonvolatile, and semivolatile; functional groups and individual species)
 - Transition metals (water soluble, bioavailable, oxidant generation)
 - Specific toxic elements and organic compounds
 - Crustal elements
 - Bioaerosols
 - Particle refractive index (real and imaginary)
 - Particle density
 - Particle size change with changes in relative humidity
-

1 A number of PM measurements are needed for use in epidemiologic and exposure studies
2 and to determine components of PM to guide planning and interpretation of toxicologic studies.
3 For these purposes, size and chemical composition measurements are important, as is
4 measurement across different time intervals. For epidemiologic studies of acute (i.e., short-term)
5 PM exposures, 1-h or continuous measurements can provide important information beyond that
6 provided by 24-h measurements. However, for epidemiologic studies of chronic PM exposures,
7 measurements that permit integration over longer intervals (e.g., a week to a month) are more
8 relevant. For dosimetric studies and modeling, information will be needed on the particle size

1 distribution and on the behavior of particles as the relative humidity and temperature changes
2 found in the atmosphere are increased to those found in the respiratory system.

3 For studies of ecological effects and materials damage, measurements of particles and of
4 the chemical components of particulate matter in rain, fog, and dew are needed to understand the
5 contributions of PM to soiling of surfaces and damage to materials and to understand the wet and
6 dry deposition of acidity and toxic substances to surface water, soil, and plants. Some
7 differentiation into particle size is needed to determine dry deposition.

8 For studies of visibility impairment and radiative effects, information is needed that relates
9 to how particles scatter and absorb light, including refractive index, ratio of scattering to
10 absorption, size distribution, and change in particle size with change in relative humidity.

11 12 **2.2.2 Issues in Measurement of Particulate Matter**

13 The EPA decision to revise the PM standards by adding daily and yearly standards for
14 $PM_{2.5}$ has led to a renewed interest in the measurement of atmospheric particles and also to a
15 better understanding of the problems in developing precise and accurate measurements of
16 particles. It is very difficult to measure and characterize particles suspended in the atmosphere;
17 however, numerous improvements in PM monitoring are in use and others are in development.
18 EPA's PM standards are based, in part, on epidemiologic relationships between health effects
19 and PM concentrations as measured with existing monitoring methods. As understanding of
20 suspended PM has advanced and new monitoring information has become available, EPA has
21 changed the indicator for the PM NAAQS from TSP to PM_{10} , and added $PM_{2.5}$. During the
22 current PM NAAQS review, consideration will be given to a standard for coarse thoracic PM.

23 The U.S. Federal Reference Methods (FRM) for $PM_{2.5}$ and PM_{10} provide relatively precise
24 ($\pm 10\%$) methods for determining the mass of material remaining on a Teflon filter after
25 equilibration. However, numerous uncertainties remain as to the relationship between the mass
26 and composition of material remaining on the filter as determined by the FRM measurement
27 procedure and the mass and composition of material that existed in the atmosphere as suspended
28 PM. As a result, EPA defines accuracy for PM measurements in terms of agreement of a
29 candidate sampler with a reference sampler. Therefore, intercomparison of samplers is very
30 important in determining how well various samplers agree and how various design choices
31 influence what is actually measured.

1 There are eight general areas where choices are made in the design and use of an aerosol
2 sampler. These include (1) consideration of positive artifacts due to chemical reaction or
3 adsorption; (2) treatment of semivolatile components; (3) selection of particle size cut
4 characteristics for the upper cut point; (4) separation of fine and coarse PM; (5) treatment of
5 pressure, temperature, and relative humidity; (6) time resolution; (7) assessment of the reliability
6 of the measurement technique; and (8) operation and maintenance procedures needed to
7 maintain consistent measurements over time. In many cases, choices have been made without
8 adequate recognition of the consequences. As a result, measurement methods developed by
9 different organizations may give different results when sampling the same atmosphere even
10 though the techniques appear to be similar.

11 12 **2.2.2.1 Artifacts Due to Chemical Reactions**

13 When TSP was collected on glass fiber filters, the reaction of SO_2 (and other acid gases)
14 with basic sites on the glass fiber or with basic coarse particles on the filter led to the formation
15 of sulfate (or other nonvolatile salts, e.g., nitrate, chloride). These positive artifacts led to
16 overestimation of mass, sulfate (and probably also of nitrate). The metal impurities in the glass
17 fiber caused a high background that led to low precision in the measurement of trace metals.
18 These problems were largely overcome by changing to quartz fiber or Teflon filters and by
19 separate collection of $\text{PM}_{2.5}$. However, the possible reaction of acidic gases with basic coarse
20 particles remains a possibility, especially with measurements of PM_{10} and $\text{PM}_{10-2.5}$. The reaction
21 of NH_3 with acidic particles, either during sampling or during transportation, storage, and
22 equilibration remains a problem in areas such as the eastern U.S. where PM is frequently acidic.
23 Techniques have been developed that overcome this problem by use of a denuder to remove NH_3
24 during sampling and to protect the collected PM from NH_3 (Suh et al., 1992, 1994; Brauer et al.,
25 1991; Koutrakis et al., 1988a,b). However, this technique has been applied primarily for
26 measurement of particle strong acidity, not for the measurement of artifact-free ammonium or
27 mass concentrations. In the measurement of particle strong acidity, basic coarse particles must
28 be separated from acidic fine particles (Koutrakis et al., 1992).

2.2.2.2 Treatment of Semivolatile Components of Particulate Matter

Current filtration-based mass measurements can experience significant evaporative losses, during and possibly after collection, of a variety of semivolatile components (i.e., species that exist in the atmosphere in dynamic equilibrium between the condensed phase and gas phase). Important examples include ammonium nitrate, semivolatile organic compounds, and particle-bound water. This problem is illustrated in Figure 2-15.

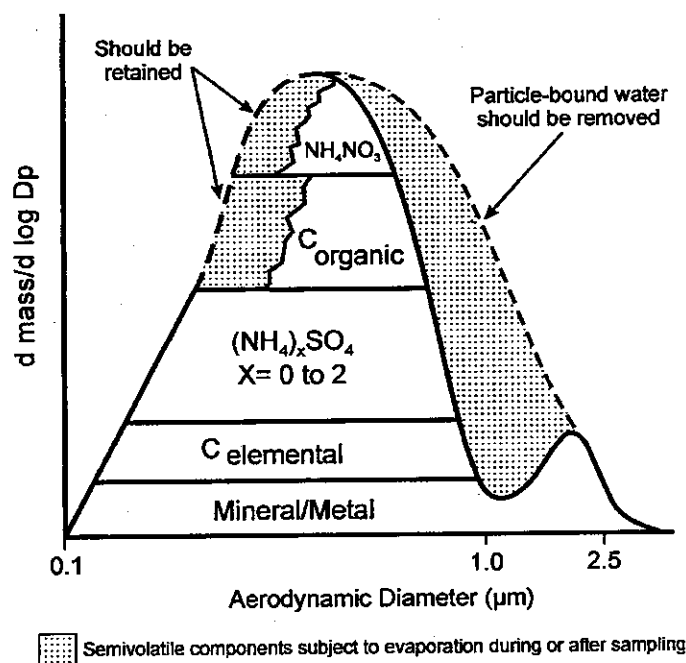


Figure 2-15. Schematic showing major nonvolatile and semivolatile components of PM_{2.5}. Semivolatile components are subject to partial to complete loss during equilibration or heating. The optimal technique would be to remove all particle-bound water but no ammonium nitrate or semivolatile organic PM.

Possible approaches that have been used to address the problem of potentially lost semivolatile components include those that follow, which will be discussed in more detail in subsequent sections.

1. Collect/measure all components present in the atmosphere in the condensed phase except particle-bound water. (Examples: Brigham Young absorptive sampler and Harvard pressure drop monitor. Both require preconcentration of the accumulation mode and reduction of ambient humidity.)
2. Stabilize PM at a specified temperature high enough to remove all, or almost all, particle-bound water. This results in loss of much of the semivolatile PM. (Examples: tapered element oscillating microbalance (TEOM) operated at 50 °C, beta gauge with heated inlet.)
3. Equilibrate collected material at fixed, near-room temperature and moderate relative humidity to reduce particle-bound water. Accept the loss of an unknown but possibly significant fraction of semivolatile PM. (Example: U.S. Federal Reference Method and most filter-weighing techniques.) Equilibration originally was designed to remove adsorbed water vapor from glass fiber filters in order to maintain a stable filter weight. The designated RH (35±5%) was a compromise. If the RH is too low, electrostatic charging becomes a problem. The equilibration process does help provide a stable and reproducible mass. It also reduces the particle-bound water. However, it may not remove all particle-bound water.

2.2.2.3 Upper Cut Point

The upper cut point of the high volume sampler varied with wind speed and direction. Newer PM samplers are usually designed to have an upper cut point and its standard deviation that are independent of wind direction and relatively independent of wind speed. Current PM samplers have upper cut points that are stable under normal operating conditions. However, problems may occur under unusual or adverse conditions. Ono et al. (2000) reported the results of a study in which several PM₁₀ samplers were collocated and operated at various sites at Owens Lake, CA, a location with high concentrations of coarse PM. Samplers included the Partisol sampler, the TEOM, a dichotomous sampler, the Wedding high-volume sampler, and the Graseby high-volume sampler. They found that the TEOM and Partisol samplers agreed to within 6% on average. The dichotomous sampler and the Graseby and Wedding high-volume

1 samplers, however, measured significantly lower PM₁₀ concentrations than the TEOM (on
2 average 10, 25, and 35% lower, respectively). These lower concentrations were attributed to a
3 decrease in the cut point at higher wind speeds and to a dirty inlet.

4 The choice of the cut point characteristics depends upon the application for the sampling
5 device. A separation that simulates the removal of particles by the human upper respiratory
6 system might appear to be a good choice for both health risk and regulatory monitoring (i.e.,
7 measure what gets into the lungs). The ACGIH-ISO-CEN penetration curve for thoracic
8 particles (particles able to pass the larynx and penetrate into the bronchial and alveolar regions of
9 the lung) has a 50% cut point at 10 µm aerodynamic diameter (D_a). The U.S. PM₁₀ separation
10 curve is sharper than the thoracic penetration curve but has the advantage of reducing the
11 problem of maintaining the finite collection efficiency specified by the thoracic penetration
12 curve for particles larger than 10 µm D_a. (See Section 2.1.2.2 and Figure 2-6).

14 2.2.2.4 Cut Point for Separation of Fine and Coarse Particulate Matter

15 As shown in Table 2-1, fine and coarse particles differ not only in size but also in
16 formation mechanisms; sources; and chemical, physical, and biological properties. They also
17 differ in concentration-exposure relationships, dosimetry (deposition and retention in the
18 respiratory system), toxicity, and health effects as observed by epidemiologic studies. Thus, it is
19 desirable to measure fine and coarse PM separately in order to properly allocate health effects to
20 either fine or coarse PM and to correctly determine sources by receptor modeling approaches.
21 For example, sulfates in fine particles are associated with hydrogen or ammonium ions while
22 sulfates in coarse particles are associated with basic metal ions. Transition metals in coarse
23 particles are likely to be associated with soil and tend to be less soluble (and presumably less
24 bioavailable) than transition metals in fresh combustion particles found in fine particles.

25 The 2.5 µm D_a cut point was chosen in the early 1970s as the cut point for a new
26 dichotomous sampler (Loo et al., 1976; Jaklevic et al., 1977) for use in the Regional Air
27 Pollution Study in St. Louis, MO. At that time aerosol scientists were beginning to realize that
28 there was a minimum between 1 and 3 µm in the distribution of particle size by volume (Whitby
29 et al., 1974). The 2.5 µm cut point was subsequently used as an indicator of fine-mode PM in a
30 number of studies including the Harvard Six-City Studies of the relationships between mortality
31 and PM concentrations (Dockery et al., 1993; Schwartz et al., 1996). A 2.5 µm cut point was

1 also used in the Inhalable Particle Network (Suggs and Burton, 1983) which provided data for
2 another major epidemiologic study of PM - mortality relationships using an American Cancer
3 Society cohort (Pope et al., 1995). Therefore, at the time of the last review of the NAAQS for
4 PM (U.S. Environmental Protection Agency, 1996a,b), there were a number of epidemiologic
5 studies demonstrating a statistical relationship between $PM_{2.5}$ concentrations and mortality.

6 It is now understood that the size range between 1.0 and 2.5 μm , sometimes called the
7 intermodal region may contain either accumulation-mode or coarse-mode material or both, i.e.,
8 the two modes may overlap in this region (Kegler et al., 2001). The experimental information on
9 the composition and source of the intermodal mass was discussed extensively in the 1996 PM
10 AQCD (U.S. Environmental Protection Agency, 1996a). Depending on conditions, a significant
11 amount of either accumulation- or coarse-mode material may be found in the intermodal region
12 between 1.0 and 2.5 μm . The analysis demonstrated the important role of relative humidity in
13 influencing the size of particles in both the accumulation and coarse modes.

14 As the relative humidity increases, hygroscopic accumulation-mode particles will increase
15 in size due to accumulation of particle-bound water. At high relative humidities, some originally
16 submicrometer accumulation-mode PM may be found with a D_a above 1 μm . At a relative
17 humidity of 100%, such as found in fog and clouds, accumulation-mode PM may extend above
18 2.5 μm D_a . What is not well understood is whether such particles will shrink to diameters below
19 1 μm as the RH decreases or whether reactions occurring in the wet particles will result in an
20 increase in non-aqueous mass so that even at low RH the diameters would exceed 1 μm . On the
21 other hand, at very low relative humidity, coarse particles may be fragmented into smaller sizes,
22 and small amounts of coarse PM may be found with an D_a below 2.5 μm (Lundgren et al., 1984;
23 Lundgren and Burton, 1995). Thus, a $PM_{2.5}$ sample will contain all of the accumulation-mode
24 PM except during periods of RH near 100 %. However, under conditions of low RH, it may also
25 contain a small fraction of the coarse PM. The selection of a cut point of 2.5 μm as a basis for
26 EPA's 1997 NAAQS for fine particles (Federal Register, 1997) and its continued use in many
27 health effects studies reflect the importance placed on more complete inclusion of accumulation-
28 mode particles while recognizing that intrusion of coarse particles can occur under some
29 conditions with this cut point.

30 In addition to the influence of relative humidity, in areas where winds cause high
31 concentrations of windblown soil there is evidence that a significant amount of coarse-mode PM

may be found below 2.5 μm . An example, taken from data collected during the August 1996 dust storm in Spokane, WA, is shown in Figure 2-16. Note that the PM_{10} scale is 10 times that of the other size fractions. PM_1 , although high in the morning, goes down as the wind increases and PM_{10} , $\text{PM}_{2.5}$, and $\text{PM}_{2.5-1}$ go up. During the peak of the dust storm, around 9 pm, $\text{PM}_{2.5-1}$ was 88% of $\text{PM}_{2.5}$. For the 24-h period, $\text{PM}_{2.5-1}$ was 54% of $\text{PM}_{2.5}$. However, PM_1 was not affected by the intrusion of coarse particles. Similar considerations probably apply to short-term intrusions of dust transported from distant sources such as the Sahara and Gobi deserts (Husar et al., 2001).

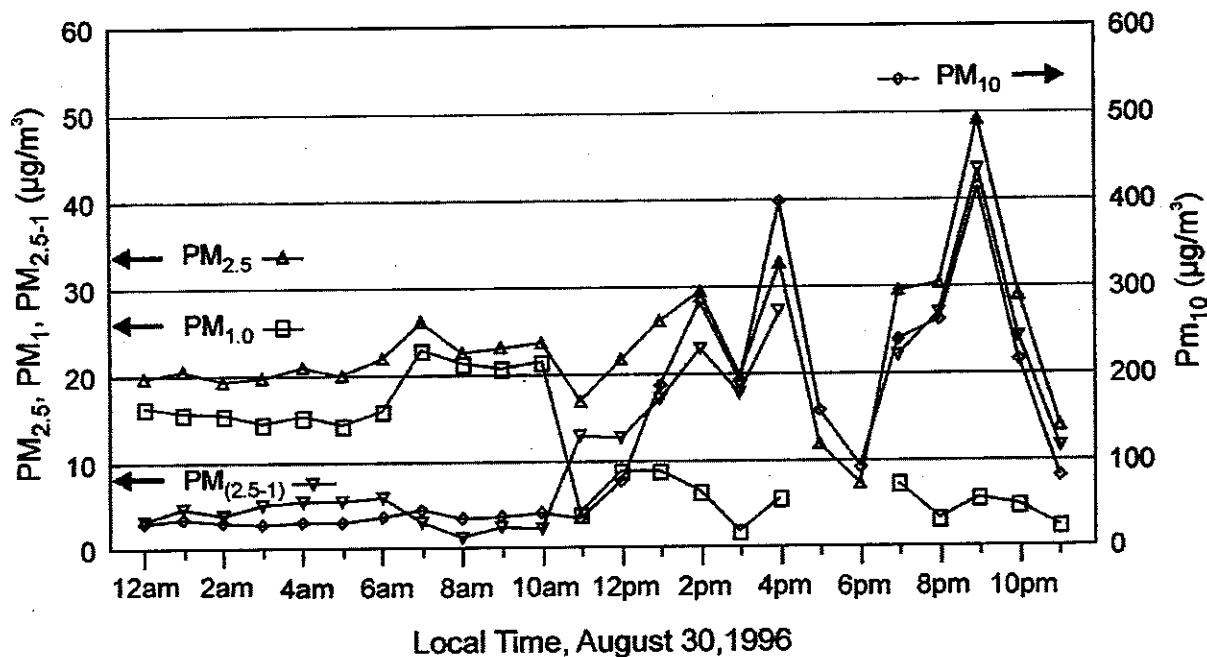


Figure 2-16. Particulate matter concentrations in Spokane, WA, during the August 30, 1996 dust storm.

Source: Claiborn et al. (2000).

A cut point of 1.0 μm could reduce the misclassification of coarse-mode material as fine, especially in areas with high levels of wind blown soil, but under high RH conditions could result in some accumulation-mode material being misclassified as coarse. A reduction in RH,

1 either intentionally or inadvertently, will reduce the mass mean diameter of the accumulation-
2 mode particles. A sufficient reduction in RH should yield a dry accumulation mode with very
3 little material above 1.0 μm . Studies of the changes in particle size with changes in relative
4 humidity suggest that only a small fraction of accumulation-mode particles will be above 1.0 μm
5 in diameter at RH below 60%, but a substantial fraction will grow above 1.0 μm for RH above
6 80% (Hitzenberger et al., 1997; McMurry and Stolzenburg, 1989; U.S. Environmental Protection
7 Agency, 1996a).

8 Under high relative humidity circumstances, a monitor using a 1.0 μm D_a cut point can
9 achieve better modal separation if the air stream is dehumidified to some fixed humidity that
10 would remove all or most particle-bound water without evaporating semivolatile components.
11 New techniques which require reduction of RH prior to collection have been developed for
12 measurement of fine particulate matter minus particle-bound water but including semivolatile
13 nitrate and organic compounds. With such techniques, PM_{10} measurements in conjunction with
14 concurrent $\text{PM}_{2.5}$ measurements would be useful for exposure, epidemiologic, and source
15 apportionment studies especially in areas where intrusion of coarse-mode particles into the
16 intermodal range is likely.

17 18 **2.2.2.5 Treatment of Pressure, Temperature, and Relative Humidity**

19 There are a variety of techniques for defining (or ignoring) the pressure, temperature, and
20 relative humidity during and after sampling. For example, the sample volume may be based on
21 the mass or volumetric flow corrected to standard temperature and pressure (273 °K and 1 atm.)
22 (current FRM for PM_{10}), or it may be based on the volumetric flow at ambient conditions of
23 temperature and pressure (current FRM for $\text{PM}_{2.5}$).

24 There are also a variety of options for the control of temperature during collection. The
25 particles may be heated enough to remove much of the particle-bound water (i.e., TEOM at
26 50 °C); the particles may be heated several degrees, just enough to prevent condensation of
27 water in the sampling system; the particles and the sampler may be maintained near ambient
28 temperature (± 5 °C of ambient temperature is required for EPA FRM samplers); or the particles
29 and sampler may be maintained at constant temperature inside a heated or air conditioned
30 shelter. There are also options for control of temperature after collection: (a) no control (room

1 temperature) or (b) ship and store at cool temperature (4 °C is the current EPA FRM
2 requirement).

3 Consideration must also be given to relative humidity. Changes in relative humidity cause
4 changes in particle size of hygroscopic or deliquescent particles. Changing relative humidity by
5 adding or removing water vapor affects measurements of particle number, particle surface area,
6 and particle size distribution and the amount of overlap of accumulation-mode and coarse-mode
7 particles. Changing relative humidity by intentional or inadvertent changes in temperature also
8 affects the amount of loss of ammonium nitrate and semivolatile organic compounds.
9 Monitoring personnel should be aware of the various options for treatment of pressure,
10 temperature, and relative humidity; make appropriate selections; and document which options
11 are used.

12 Studies of relationships between personal/indoor/outdoor measurements present special
13 problems. Indoor environments are typically dryer than outdoors and may be warmer or, if
14 air-conditioned, cooler. These differences may change particle size and the amount of
15 volatilization of semivolatile components. Such changes between indoors and outdoors will
16 complicate the comparison of indoor to outdoor PM concentrations; the modeling of personal
17 exposure to all particles; and apportionment of personal exposure into particles of ambient
18 origin, particles of indoor origin, and particles originating from personal activity.

19 20 **2.2.2.6 Time Resolution**

21 The classic 24-hour filter collection technique is being supplemented by a variety of
22 continuous monitors for various PM constituents. This process is being accelerated by the lower
23 operational cost of continuous monitors and the availability of new continuous monitors for
24 mass, number, and certain chemical components, as well as refinements of older methods based
25 on beta attenuation or light scattering. Most epidemiologic studies have used 24-hour
26 concentrations as exposure indicators. However, one epidemiologic study of chronic effects
27 uses a filter sampler with a two-week collection period (Gauderman et al., 2000). Another
28 recent study used 1-2 h concentrations (see Peters et al., 2000). Continuous methods are
29 discussed in Section 2.2.5.

2.2.2.7 Accuracy and Precision

Precision is typically determined by comparison of collocated samplers or through replicate analyses; whereas accuracy is determined through the use of traceable calibration standards. Unfortunately, no standard reference calibration material or procedure has been developed for suspended, atmospheric PM. It is possible to determine the accuracy of certain components of the PM measurement system (e.g., flow control, inlet aspiration, PM_{2.5} cut, weighing, etc.). The absolute accuracy for collecting a test aerosol can also be determined by isokinetic sampling in a wind tunnel. However, it is not currently feasible to provide a simulated atmospheric aerosol with naturally occurring semivolatile components. It is particularly challenging to develop an atmospheric aerosol calibration standard suitable for testing samplers in the field. Therefore, it is not possible at the present time to establish the absolute accuracy of a PM monitoring technique. Intercomparison studies may be used to establish the precision of identical monitors and the extent of agreement between different types of monitors. Such studies are important for establishing the reliability of PM measurements. Intercomparison studies have contributed greatly to our understanding of the problems in PM measurement. Such studies will be discussed as they apply to specific measurement problems, monitoring instruments, or analytical techniques.

Some measurement errors of concern in PM₁₀ sampling, including those that arise due to uncertainty tolerances in cutpoint, particle bounce and reentrainment, impactor surface overloading, and losses to sampler internal surfaces, were discussed in detail in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a). Other measurement errors of concern in PM_{2.5} sampling arise because of our inability to assess accuracy in an absolute sense due to a lack of an atmospheric aerosol calibration standard, the inclusion in PM_{2.5} of a small amount of coarse particles as discussed in Section 2.2.1.3, problems associated with the definition of PM_{2.5} as what remains on a filter after collection and equilibration rather than as the mass of particles as they exist in the air. Still, it is possible to measure PM indicators with high precision. Detailed information on precision and quality assurance may be found on EPA's Technology Transfer Network website (U.S. Environmental Protection Agency, 2002a). See discussion in Section 2.2.4.

Because of the difficulties associated with determining the accuracy of PM measurements, EPA has sought to make FRM measurements equivalent by specifying operating conditions and,

1 in the case of PM_{2.5} samplers, by specifying details of the sampler design. Thus, both the PM₁₀
2 as well as the PM_{2.5} standards are defined with consistency of measurement technique rather than
3 with the accuracy of the true mass concentration measurement in mind (McMurry, 2000). It is
4 acknowledged in the Federal Register (1997) that, "because the size and volatility of the particles
5 making up ambient particulate matter vary over a wide range and the mass concentration of
6 particles varies with particle size, it is difficult to define the accuracy of PM_{2.5} measurements in
7 an absolute sense...." Thus, accuracy is defined as the degree of agreement between a field
8 PM_{2.5} sampler and a colocated PM_{2.5} reference method audit sampler (McMurry, 2000). The
9 Federal Reference Method for PM_{2.5} is discussed in Section 2.2.3.3. As mentioned earlier,
10 volatilization of organic compounds and ammonium nitrate during sampling or post-sampling
11 handling can lead to significant underestimation of the fine particulate mass concentration in
12 some locations. Sources of error in the measurement of mass of PM_{2.5} suspended in the
13 atmosphere also arise because of adsorption or desorption of semivolatile vapors onto or from
14 collected PM, filter media, or other sampler surfaces; neutralization of acid or basic vapors on
15 either filter media or collected PM; and artifacts associated with particle-bound water.

16 During the past 25 years, there have been advancements in the generation and
17 classification of monodisperse aerosols as well as in the development of electron microscopy and
18 imaging analysis that have contributed to the advancement in aerosol calibration (Chen, 1993).
19 Still, one of the limitations in PM sampling and analysis remains the lack of primary calibration
20 standards for evaluating analytical methods and for intercomparing laboratories. Klouda et al.
21 (1996) examined the possibility of resuspending the National Institute of Science and
22 Technology (NIST) Standard Reference Material 1649 (Urban Dust) in air for collection on up to
23 320 filters simultaneously using Standard Research International's dust generation and collection
24 system. However, the fine component is not resuspended and the semivolatile component has
25 evaporated. Consequently, this material is not a suitable standard for suspended PM. NIST is
26 continuing work in this area with EPA support.

27 Methods validation was discussed in the 1996 PM AQCD (U.S. Environmental Protection
28 Agency, 1996a), and the usefulness of intercomparisons and "internal redundancy" was
29 emphasized. For example, a number of internal consistency checks are applied to the IMPROVE
30 network (Malm et al., 1994). These include mass balances, sulfur measurements by both
31 proton-induced X-ray emission (PIXE) and ion chromatography (IC), and comparison of organic

1 matter by combustion and by proton elastic scattering (PESA) of hydrogen. Mass balances
2 compare the gravimetrically determined mass with the mass calculated from the sum of the
3 major chemical components (i.e., crustal elements plus associated oxygen, organic carbon,
4 elemental carbon, sulfate, nitrate, ammonium, and hydrogen ions). Mass balances are useful
5 validation techniques; however, they do not check for, or account for, artifacts associated with
6 the absorption of gases during sampling or the loss of semivolatile material during sampling.
7 The mass balance check may appear reasonable even if such artifacts are present because only
8 the material collected on the filter is included in the balance. Mass balance checks may also
9 suffer from errors due to some particle-bound water remaining in the PM even after equilibration
10 and from the use of an arbitrary factor to account for the amount of oxygen and hydrogen atoms
11 per carbon atom in the organic carbon fractions (Andrews et al., 2000).

12 13 **2.2.3 Measurement of Semivolatile Particulate Matter**

14 PM suspended in the atmosphere is composed of many chemical species having a wide
15 range of vapor pressures. Substances with vapor pressures below 10^{-9} Torr (mmHg) will
16 typically be nonvolatile; substances with vapor pressures above 10^{-1} Torr will be primarily in the
17 gas phase; substances with vapor pressures between 10^{-1} and 10^{-9} Torr may exist in an
18 equilibrium state with some material in both the gas phase and the condensed (particulate) phase
19 and are known semivolatile material (SVM) (Pankow, 1994a). SVM, originally in the
20 atmosphere in the particulate phase and collected on a filter, may subsequently be lost from the
21 filter. SVM may evaporate during sampling due to a reduction in its concentration in the
22 atmosphere being sampled or due to the pressure drop across the filter. SVM may evaporate
23 after sampling; during intentional equilibration at a low relative humidity; or during transport,
24 handling, and storage if exposed to an atmosphere in which the vapor pressure of one or more
25 semivolatile components is lower than in the atmosphere sampled. Since water is not a
26 pollutant, it is necessary to remove most of the particle-bound water before weighing (Chow,
27 1995). However, collection and measurement of ammonium nitrate and semivolatile organic
28 compounds in suspended atmospheric PM represents a major analytical challenge (McMurry,
29 2000).

2.2.3.1 Particle-Bound Water

It is generally desirable to collect and measure ammonium nitrate and semivolatile organic compounds. However, for many measurements of suspended particle mass, it is desirable to remove the particle-bound water before determining the mass. The mass of particle-bound water is strongly dependent on the relative humidity. However, the dependence is not linear since there is significant hysteresis in the water adsorption-desorption pathways (Seinfeld and Pandis, 1998). Water vapor is not a pollutant and cannot be controlled. Particle-bound water is not included in the mass of PM subject to regulation and control. Because the mass of particle-bound water could be equal or greater than that of the other components, a measurement of PM mass including particle-bound water would depend more on relative humidity than pollution. For all these reasons, it is usually desirable to remove most, if not all, particle-bound water before weighing collected PM. However, in some situations it may be important to know how much of the suspended particle's mass or volume results from particle-bound water. Figures 2-13 and 2-14 show the change in diameter of sulfate particles as a function of relative humidity. Figure 2-13 also shows hysteresis resulting from the difference between deliquescence and crystallization points.

Pilinis et al. (1989) calculated the water content of atmospheric particulate matter above and below the deliquescent point. They predicted that aerosol water content is strongly dependent on composition and concluded from their calculations that liquid water could represent a significant mass fraction of aerosol concentration at relative humidities above 60%. Since then, a few researchers have attempted to measure the water content of atmospheric aerosol. Most techniques have focused on tracking the particle mass as the relative humidity is changed and are still in the development phase. There have been only a few demonstrations using actual ambient aerosol to date. Of interest, in particular, is the development of the Tandem Differential Mobility Analyzer (TDMA) and its applications in investigations of the effects of relative humidity on particle growth.

Lee et al. (1997) examined the influence of relative humidity on the size of atmospheric aerosol using a TDMA coupled with a scanning mobility particle sizer (SMPS). They reported that the use of the TDMA/SMPS system allowed for the abrupt size changes of aerosols at the deliquescence point to be observed precisely. They also reported that at relative humidities

1 between 81 and 89% the water content of ammonium sulfate aerosols (by mass) ranged from
2 47 to 66%.

3 Andrews and Larson (1993) investigated the interactions of single aerosol particles coated
4 with an organic film within a humid environment. Using an electrodynamic balance, they
5 conducted laboratory experiments in which sodium chloride and carbon black particles were
6 coated with individual organic surfactants (intended to simulate the surface-active, organic films
7 that many atmospheric aerosol particles may exhibit) and their water sorption curves were
8 examined. Their results showed that when ordinarily hydrophobic carbon black particles were
9 coated with an organic surfactant, they sorbed significant amounts of water (20 to 40% of the dry
10 mass of the particle).

11 Liang and Chan (1997) developed a fast technique using the electrodynamic balance to
12 measure the water activity of atmospheric aerosols. In their technique, the mass of a levitated
13 particle is determined as the particle either evaporates or grows in response to a step change in
14 the relative humidity. Their technique was demonstrated using laboratory experiments with
15 NaCl, $(\text{NH}_4)_2\text{SO}_4$, NaNO_3 , and $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{NO}_3$ solutions. They concluded that one of the
16 advantages of their fast method is the ability to measure the water activity of aerosols containing
17 volatile solutes such as ammonium chloride and some organics.

18 McInnes et al. (1996) measured aerosol mass concentration, ionic composition, and
19 associated water mass of marine aerosol over the remote Pacific Ocean. The mass of
20 particle-bound water was determined by taking the difference between the mass obtained at 48%
21 RH and at 19% RH, assuming the aerosol particles were dry at 19% RH. Based on a comparison
22 of the remote Pacific aerosol to aerosol collected at a site at the marine/continental interface of
23 the Washington coast, the amount of water associated with the aerosol was observed to be a
24 function of the ammonium to sulfate ratio. They found that the amount of water associated with
25 the submicrometer aerosol comprised 29% of the total aerosol mass collected at 47% RH and
26 9% of the total mass at 35% RH.

27 Ohta et al. (1998) characterized the chemical composition of atmospheric fine particles
28 (50% cut point of 2 μm) in Sapporo, Japan, and as part of their measurements, determined the
29 water content using the Karl Fischer method (Meyer and Boyd, 1959). After exposing a Teflon
30 filter, a portion of the filter was equilibrated at 30% RH for 24 h. Then the filter piece was
31 placed in a water evaporator heated at 150 °C, vaporizing the particle-bound water. The vapor

1 evolved was analyzed for water in an aqua-counter where it was titrated coulometrically in Karl
2 Fischer reagent solution (containing iodine, sulfur, and methanol). The accuracy of the aqua-
3 counter is ± 1 mg. Using this technique, they determined that the water content of the particles
4 ranged from 0.4 to 3.2% of the total particulate mass (at RH < 30%). This represents a smaller
5 portion of water compared to their previous reported values (Ohta and Okita, 1990) that were
6 determined by calculation at RH of 50%.

7 Speer et al. (1997) developed an aerosol liquid water content analyzer (LWCA) in which
8 aerosol samples are collected on PTFE filters and then placed in a closed chamber in which the
9 relative humidity is closely controlled. The aerosol mass is monitored using a beta-gauge, first
10 as the relative humidity is increased from low RH to high RH, and then as the RH is decreased
11 again. They demonstrated the LWCA on laboratory-generated aerosol and on an ambient PM_{2.5}
12 sample collected in Research Triangle Park, NC. The ambient aerosol sample was also analyzed
13 for chemical constituents. It is interesting to note that, although their laboratory-generated
14 (NH₄)₂SO₄ aerosol demonstrated a sharp deliquescent point, their atmospheric aerosol, which
15 was essentially (NH₄)₂SO₄, did not show a sharp deliquescent point.

16 Hygroscopic properties of aerosols have been studied from the viewpoint of their ability to
17 act as condensation nuclei. The hygroscopic properties of fresh and aged carbon and diesel soot
18 particles were examined by Weingartner et al. (1997) who found that fresh, submicron-size
19 particles tended to shrink with increasing relative humidity because of a structural change.
20 Lammel and Novakov (1995) found, in laboratory studies, that the hygroscopicity of soot
21 particles could be increased by chemical modification and that the cloud condensation nucleation
22 characteristics of diesel soot were similar to those of wood smoke aerosol.

23 The results of several of the above studies in which aerosol water content as a function of
24 relative humidity was determined are summarized in Figure 2-17. In this figure, the results of
25 Lee et al. (1997), McInnes et al. (1996), and Ohta et al. (1998) are included. Relative humidity
26 ranged from 9%, at which the aerosol water content was assumed to be zero (McInnes et al.,
27 1996), to 89%, at which the aerosol water content was determined to be 66% by mass (Lee et al.,
28 1997). Koutrakis et al. (1989) and Koutrakis and Kelly (1993) also have reported field
29 measurements of the equilibrium size of atmospheric sulfate particles as a function of relative
30 humidity and acidity.

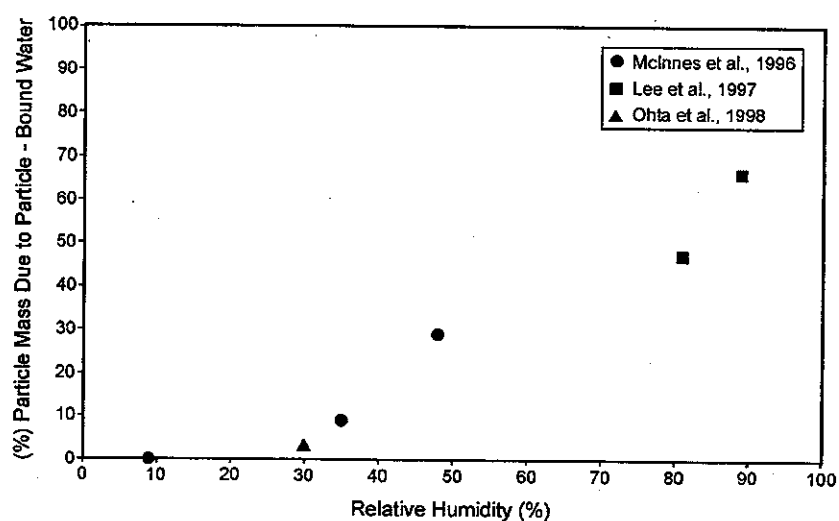


Figure 2-17. Aerosol water content expressed as a mass percentage, as a function of relative humidity.

The effects of relative humidity on particle growth were also examined in several studies. Fang et al. (1991) investigated the effects of flow-induced relative humidity changes on particle cut sizes for aqueous sulfuric acid particles in a multi-nozzle micro-orifice uniform deposit impactor (MOUDI). Laboratory experiments were conducted in which polydisperse sulfuric acid aerosols were generated and the RH was adjusted. The aerosols were analyzed by a differential mobility analyzer. Fang et al. (1991) observed that for inlet RH less than 80%, the cut sizes for the sulfuric acid aerosols were within 5% of that for nonhygroscopic particles except at the stage for which the cut size was $0.047 \mu\text{m}$ where the cut size was 10.7% larger than the nonhygroscopic particle cut size. They concluded that flow-induced RH changes would have only a modest effect on MOUDI cut sizes at $\text{RH} < 80\%$.

Hitzenberger et al. (1997) collected atmospheric aerosol in the size range of 0.06 to $15 \mu\text{m}$ in Vienna, Austria, using a nine-stage cascade impactor and measured the humidity-dependent water uptake when the individual impaction foils were exposed to high RH. They observed particle growth with varying growth patterns. Calculated extinction coefficients and single scattering albedo increased with humidity.

Hygroscopic properties, along with mixing characteristics, of submicrometer particles sampled in Los Angeles, CA, during the summer of 1987 SCAQS study and at the Grand

1 Canyon, AZ, during the 1990 Navajo Generating Station Visibility Study were reported by
2 Zhang et al. (1993). They used a tandem differential mobility analyzer (TDMA; McMurry and
3 Stolzenburg, 1989) to measure the hygroscopic properties for particles in the 0.05- to 0.5- μ m
4 range. In their experimental technique, monodisperse particles of a known size are selected from
5 the atmospheric aerosol with the first DMA. Then, the relative humidity of the monodisperse
6 aerosol is adjusted, and the new particle size distribution is measured with the second DMA.
7 At both sites, they observed that monodisperse particles could be classified according to "more"
8 hygroscopic and "less" hygroscopic. Aerosol behavior observed at the two sites differed
9 markedly. Within the experimental uncertainty ($\pm 2\%$) the "less" hygroscopic particles sampled
10 in Los Angeles did not grow when the RH was increased to 90%; whereas at the Grand Canyon,
11 the growth of the "less" hygroscopic particles varied from day to day, but ranged from near 0 to
12 40% when the RH was increased to 90%. The growth of the "more" hygroscopic particles in
13 Los Angeles was dependent on particle size (15% at 0.05 μ m to 60% at 0.5 μ m); whereas at the
14 Grand Canyon, the "more" hygroscopic particles grew by about 50% with the growth not
15 varying significantly with particle size. By comparison of the TDMA data to impactor data,
16 Zhang et al. (1993) surmised that the more hygroscopic particles contained more sulfates and
17 nitrates while the less hygroscopic particles contained more carbon and crustal components.

18 Although most of the work to date on the hygroscopic properties of atmospheric aerosols
19 has focused on the inorganic fraction, the determination of the contribution of particle-bound
20 water to atmospheric particulate mass is greatly complicated by the presence of organics. The
21 effect of RH on adsorption of semivolatile organic compounds is discussed elsewhere in this
22 chapter. Saxena et al. (1995) observed that particulate organic compounds also can affect the
23 hygroscopic behavior of atmospheric particles. They idealized the organic component of aerosol
24 as containing a hydrophobic fraction (high-molecular weight alkanes, alkanolic acids, alkenolic
25 acids, aldehydes, and ketones) and a hydrophilic fraction (e.g., lower molecular weight
26 carboxylic acids, dicarboxylic acids, alcohols, aldehydes, etc.) that would be likely to absorb
27 water. They then analyzed data from a tandem differential mobility analyzer in conjunction with
28 particle composition observations from an urban site (Claremont, CA) and from a nonurban site
29 (Grand Canyon) to test the hypothesis that, by adding particulate organics to an inorganic
30 aerosol, the amount of water absorbed would be affected, and the effect could be positive or
31 negative, depending on the nature of the organics added. They further presumed that the

1 particulate organic matter in nonurban areas would be predominantly secondary and thus
2 hydrophilic, compared to the urban aerosol that was presumed to be derived from primary
3 emissions and thus hydrophobic in nature. Their observations were consistent with their
4 hypothesis, in that at the Grand Canyon, the presence of organics tended to increase the water
5 uptake by aerosols; whereas at the Los Angeles site, the presence of organics tended to decrease
6 water uptake.

7 Peng and Chan (2001) also recently studied the hygroscopic properties of nine water
8 soluble organic salts of atmospheric interest using an electrodynamic balance operated at 25°C.
9 Salts studied included sodium formate, sodium acetate, sodium succinate, sodium pyruvate,
10 sodium methanesulfonate, sodium oxalate, ammonium oxalate, sodium malonate, and sodium
11 maleate. They observed that hygroscopic organic salts have a growth factor of 1.76-2.18 from
12 RH=10-90%, comparable to that of typical hygroscopic inorganic salts such as NaCl and
13 $(\text{NH}_4)_2\text{SO}_4$.

14 Nonequilibrium issues may be important for the TDMA, as well as for other methods of
15 measuring water content. Although approach to equilibrium when the RH is increased is
16 expected to be rapid for pure salts, it may be much slower for aerosols containing a complex mix
17 of components (Saxena et al., 1995). For example, if an aerosol contains an organic film or
18 coating, that film may impede the transport of water across the particle surface, thus increasing
19 the time required for equilibrium (Saxena et al., 1995). Insufficient time to achieve equilibrium
20 in the TDMA could result in underestimation of the water content.

22 2.2.3.2 Nitrate and Organic Species

23 *Particulate Nitrates*

24 It is now well known that volatilization losses of particulate nitrates occur during sampling
25 on Teflon filters (e.g., Zhang and McMurry [1992]; see also Hering and Cass [1999] and Babich
26 et al., [2000]). The effect on the accuracy of atmospheric particulate measurements from these
27 volatilization losses is more significant for $\text{PM}_{2.5}$ than for PM_{10} . The FRM for $\text{PM}_{2.5}$ will likely
28 suffer loss of nitrates similar to that experienced with other simple filter collection systems.
29 Sampling artifacts resulting from the loss of particulate nitrates represents a significant problem
30 in areas such as southern California that experience high amounts of nitrates. Hering and Cass
31 (1999) reported on errors in $\text{PM}_{2.5}$ mass measurements due to volatilization of particulate nitrate

(Figure 2-18). They examined data from two field measurement campaigns conducted in southern California: (1) the Southern California Air Quality Study (SCAQS) (Lawson, 1990) and (2) the 1986 CalTech study (Solomon et al., 1992). In both these studies, side-by-side sampling of $PM_{2.5}$ was conducted. One sampler collected particles directly onto a Teflon filter. The second sampler consisted of a denuder to remove gaseous nitric acid followed by a nylon filter that absorbs the HNO_3 which evaporates from ammonium nitrate. In both studies, the denuder consisted of MgO-coated glass tubes (Appel et al., 1981). Fine particulate nitrate collected on the Teflon filter was compared to fine particulate nitrate collected on the denuded nylon filter. In both studies, the $PM_{2.5}$ mass lost because of volatilization of ammonium nitrate represented a significant fraction of the total $PM_{2.5}$ mass. The fraction of mass lost was higher during summer than during fall (17% versus 9% during the SCAQS study and 21% versus 13% during the CalTech study; Figure 2-18). In regard to percentage loss of nitrate, as opposed to percentage loss of mass discussed above, Hering and Cass (1999) found that nitrate remaining on the Teflon filter samples was on average 28% lower than that on the denuded nylon filters.

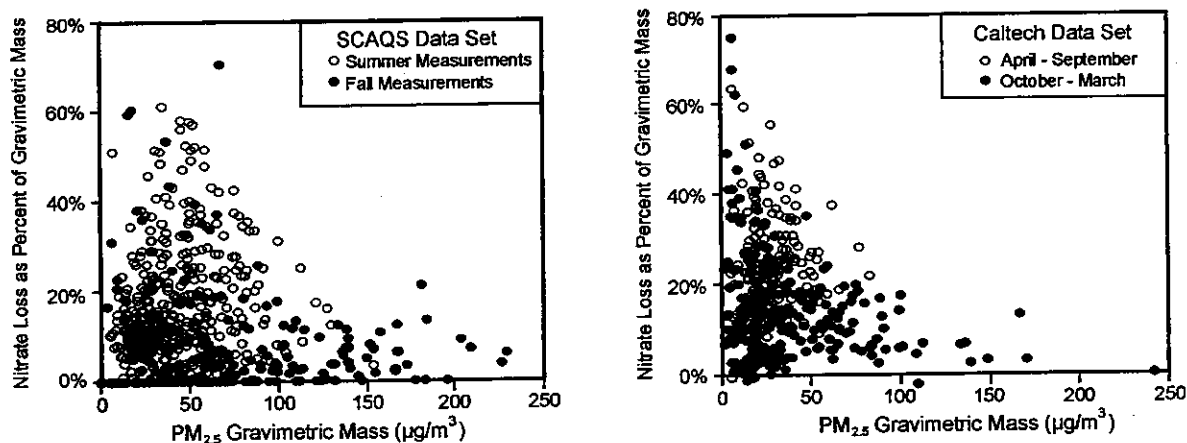


Figure 2-18. Amount of ammonium nitrate volatilized from Teflon filters, expressed as a percentage of the measured $PM_{2.5}$ mass, for the SCAQS and CalTech studies, for spring and fall sampling periods.

Source: Hering and Cass (1999).

1 Hering and Cass (1999) also analyzed these data by extending the evaporative model
2 developed by Zhang and McMurry (1987). The extended model utilized by Hering and Cass
3 (1999) takes into account dissociation of collected particulate ammonium nitrate on Teflon
4 filters into nitric acid and ammonia via three mechanisms: (1) scrubbing of nitric acid and
5 ammonia in the sampler inlet (John et al., 1988 showed that clean PM_{10} inlet surfaces serve as an
6 effective denuder for nitric acid), (2) heating of the filter substrate above ambient temperature by
7 sampling, and (3) pressure drop across the Teflon filter. For the sampling systems modeled, the
8 flow-induced pressure drop was measured to be less than 0.02 atm, and the corresponding
9 change in vapor pressure was 2%, so losses driven by pressure drop were not considered to be
10 significant in this work. Losses from Teflon filters were found to be higher during the summer
11 compared to the winter, higher during the day compared to night, and reasonably consistent with
12 modeled predictions.

13 Finally, during the SCAQS study, particulate samples also were collected using a Berner
14 impactor and greased Tedlar substrates in size ranges from 0.05 to 10 μm in aerodynamic
15 diameter. The Berner impactor $PM_{2.5}$ nitrate values were much closer to those from the denuded
16 nylon filter than those from the Teflon filter with the impactor nitrate being approximately
17 2% lower than the nylon filter nitrate for the fall measurements and approximately 7% lower
18 during the summer measurements. When the impactor collection was compared to the Teflon
19 filter collection for a nonvolatile species (sulfate), the results were in agreement.

20 It should be noted that filters or collection surfaces were removed immediately after
21 sampling and placed into vials containing a basic extraction solution during these
22 intercomparison studies. Therefore, losses that might occur during handling, storage, and
23 equilibration of filters or impaction surfaces were avoided. The loss of nitrate observed from
24 Teflon filters and impaction surfaces in this study, therefore, is a lower limit compared to losses
25 that might occur during the normal processes involved in equilibration and weighing of filters
26 and impaction surfaces. Brook and Dann (1999) observed much higher nitrate losses during a
27 study in which they measured particulate nitrate in Windsor and Hamilton, Ontario, Canada, by
28 three techniques: (1) a single Teflon filter in a dichotomous sampler, (2) the Teflon filter in an
29 annular denuder system (ADS), and (3) total nitrate including both the Teflon filter and the
30 nylon back-up filter from the ADS. The Teflon filter from the dichotomous sampler averaged
31 only 13% of the total nitrate. The Teflon filter from the ADS averaged 46% of the total nitrate.

1 The authors concluded that considerable nitrate was lost from the dichotomous sampler filters
2 during handling, which included weighing and x-ray fluorescence (XRF) measurement in a
3 vacuum.

4 Kim et al. (1999) also examined nitrate sampling artifacts by comparing denuded and
5 undenuded quartz and nylon filters, during the PM₁₀ Technical Enhancement Program (PTEP) in
6 the South Coast Air Basin of California. They observed negative nitrate artifacts (losses) for
7 most measurements; however, for a significant number of measurements they observed positive
8 nitrate artifacts. Kim et al. (1999) pointed out that random measurement errors make it difficult
9 to measure true amounts of nitrate loss.

10 Diffusion denuder samplers, developed primarily to measure particle strong acidity
11 (Koutrakis et al., 1988a,b, 1992), also can be used to study nitrate volatilization. Such
12 techniques were used to measure loss of particulate nitrate from Teflon filters in seven U.S.
13 cities (Babich et al., 2000). Measurements were made with two versions of the Harvard-EPA
14 Annular Denuder System (HEADS). Nitric acid vapor was removed by a Na₂CO₃-coated
15 denuder. Particulate nitrate was the sum of nonvolatile nitrate collected on a Teflon filter and
16 volatilized nitrate collected on a Na₂CO₃-coated denuder downstream of the Teflon filter (full
17 HEADS) or on a Nylon filter downstream of the Teflon filter (Nylon HEADS). It was found that
18 full HEADS (using a Na₂CO₃ denuder) consistently underestimated the total particulate nitrate
19 by approximately 20% compared to the nylon HEADS. Nonvolatilized nitrate was also
20 measured on a Teflon filter from colocated Harvard Impactors (HI). The PM_{2.5} HI sampler, like
21 the PM_{2.5} FRM, use impactors with a 50% cut at 2.5 µm. The HI uses a 37 mm filter and a flow
22 rate of 10 L/min (0.465 L/min/cm²) which the FRM uses a 47 mm filter and a flow rate of 16.7
23 L/min (0.481 L/min/cm²). Therefore, the flow rate and pressure drop across the filters are
24 similar and the loss of nitrate should be similar in both types of samples. Babich et al. (2000)
25 found significant nitrate losses in Riverside, CA; Philadelphia, PA; and Boston, MA but not in
26 Bakersfield, CA; Chicago, IL; Dallas, TX; or Phoenix, AZ where measurements were made only
27 during winter.

28 Eatough et al. (1999a) developed a high-volume diffusion denuder system in which
29 diffusion denuder and particle concentrator techniques were combined (see Section 2.2.3.2). The
30 particle concentrator reduces the flow through the denuder so that the denuder can be operated
31 for weeks without a loss of collection efficiency, making the sampler suitable for routine field

1 sampling. The system was evaluated for the collection of fine particulate sulfate and nitrate in
2 Riverside, CA (Eatough et al., 1999b). Concentrations of PM_{2.5} nitrate obtained from the PC-
3 BOSS agreed with those obtained using the Harvard-EPA Annular Denuder Sampler, HEADS
4 (Koutrakis et al., 1988b).

6 *Particulate Organic Compounds*

7 Many semivolatile organic compounds (SVOC) are of interest because of their possible
8 health effects. SVOC include products of incomplete combustion such as polycyclic aromatic
9 hydrocarbons (PAHs) and polycyclic organic matter, which has been identified as a hazardous
10 air pollutant. PAHs also have been suggested as alternative particulate tracers for automobile
11 emissions because the phase-out of organo-lead additives to gasoline means that lead is no
12 longer a good tracer for automobiles (Venkataraman et al., 1994). PAHs also are emitted during
13 biomass burning, including burning of cereal crop residues and wood fuels (Jenkins et al., 1996;
14 Roberts and Corkill, 1998).

15 A number of studies have used absorbing material following quartz filters to determine
16 phase equilibria of specific organic compounds (Liang et al., 1997; Gundel et al., 1995; Kamens
17 et al., 1995). Much work has also gone into the development of a theory to help understand the
18 phase relationships (Yamasaki et al., 1982; Rounds and Pankow, 1990; Pankow, 1987, 1994a,b;
19 Pankow et al., 1993; Rounds et al., 1993; Odum et al., 1994). The theory describing phase
20 equilibria of semivolatile organic compounds (SVOC) and the gas/particle partitioning of SVOC
21 on inorganic, organic, and ambient smog aerosols continues to be developed (Liang et al., 1997;
22 Jang et al., 1997, 1999; Strommen and Kamens, 1997; Jang and Kamens, 1998, 1999, 2001;
23 Leach et al., 1999; Kamens et al., 1999, 2001).

24 The mass of organic and elemental carbon is usually determined by analysis of PM
25 collected on a quartz filter. However, quartz fiber filters have a large specific surface area on
26 which adsorption of gases can occur. Possible artifacts associated with adsorption of organic
27 gases onto quartz filters have been examined in experiments in which two quartz fiber filters
28 were deployed in series. The second quartz filter may indicate gaseous volatile organic
29 compounds (VOC) adsorbed on both filters (positive artifact), SVOC evaporated from particles
30 on the first filter and subsequently adsorbed on the second filter (negative artifact), or a
31 combination of both effects. Unless the individual compounds are identified, the investigator

1 does not know what to do with the loading value on the second filter (i.e., to add or subtract from
2 the first filter loading value). Moreover, even if the individual compounds were identified on the
3 back-up filter, the decision concerning adding or subtracting the back-up filter loading would not
4 be straightforward.

5 The positive quartz filter artifact has been discussed by Gundel et al. (1995) and Turpin
6 et al. (2000). It is also possible that some SVOC may desorb from the filter resulting in a
7 negative artifact (Eatough et al., 1993; Tang et al., 1994; Eatough et al., 1995; Gundel et al.,
8 1995; Cui et al., 1998; Pang et al., 2001; Finn et al., 2001). Semivolatile organic compounds can
9 similarly be lost from Teflon filters because of volatilization, causing the $PM_{2.5}$ mass to be
10 significantly underestimated (negative artifact). Like particulate nitrates, the FRM for $PM_{2.5}$ will
11 suffer loss of SVOC, similar to the losses experienced with other simple filter collection
12 systems. Most studies that have focused on the positive and negative sampling artifacts
13 associated with SVOC compounds have utilized either diffusion denuder technology (Eatough
14 et al., 1995; Mader et al., 2001) or placed an adsorbent media, such as a back-up quartz filter or a
15 polyurethane foam adsorbent behind the main filter (Wallace and Hites, 1995). Further
16 information on denuder techniques are given in Appendix 2A.

17 Using their multichannel diffusion denuder sampling system (BOSS), Eatough et al. (1995)
18 reported that, for samples collected at the South Coast Air Quality Management District
19 sampling site at Azusa, CA, changes in the phase distribution of SVOC could result in a loss on
20 average of 35% of the particulate organic material. Cui et al. (1998) found that losses of SVOC
21 from particles in the Los Angeles Basin during the summer were greater during the night
22 (average = 62%) than during the day (average = 42%).

23 The percent SVOC lost from the front filter in a filter-denuder system may be greater than
24 that lost in a filter-only system such as the FRM. In a filter-denuder system, the gas-phase
25 component of the SVOC is removed. The absence of the gas-phase causes the gas-particle
26 equilibrium to shift so the SVOC collected on the filter may evaporate more rapidly in a filter-
27 denuder system than in a filter-only collection system. To determine the fraction of SVOC lost
28 from a Teflon filter in a filter-only system, it is necessary to compare the amount measured by a
29 nondenuder system with that measured by a denuder system. At present, little information is
30 available on the volatilization losses of SVOC. However, in one study (Pang et al., 2001), the
31 total mass on denuded and undenuded filters were compared and found to be identical within

1 error limits ($R^2 = 0.816$, slope = 0.961 ± 0.027 for total mass compared to $R^2 = 0.940$, slope =
2 0.986 ± 0.020 for sulfate). Pang et al. interpreted this result as suggesting that the major cause of
3 loss of SVOC is the pressure drop across the filter.

4 Positive artifacts may occur during sample collection because of the adsorption of gases
5 onto the filter materials (e.g., Gundel et al., 1995). Using a quartz filter behind a Teflon filter,
6 Kim et al. (2001a) estimated that on an annual average basis 30% of the $PM_{2.5}$ organic carbon
7 concentration resulted from positive artifacts. There is a larger positive artifact because of
8 greater adsorption of organic vapor onto quartz fiber filters than onto Teflon filters (Turpin et al.,
9 1994; Chow et al., 1994a,b, 1996; Eatough et al., 1996; Finn et al., 2001; Kirchstetter et al.,
10 2001).

11 Kirchstetter et al. (2001) report that adsorptive properties of quartz fiber filters vary with
12 lot number; therefore, front and back-up filters should be taken from the same lot. The literature
13 suggests that a Teflon filter followed by a quartz back-up filter appears to provide a better
14 estimate of the adsorption of gases on a quartz fiber front filter than does a quartz filter followed
15 by a quartz backup and that the difference between these two adsorption estimates can be
16 substantial for short durations (Novakov et al., 1997; Kirchstetter et al., 2001; Turpin et al.,
17 2000). The typically lower organic carbon loadings on concurrently collected quartz followed
18 by quartz filters relative to Teflon followed by quartz filters are believed to occur because
19 adsorption on the quartz front filter acts to reduce the gas-phase concentration downstream until
20 adsorption equilibrium has been achieved in the vicinity of the front quartz filter surface.
21 Because Teflon filters have little affinity for organic vapors, this equilibrium occurs almost
22 instantaneously for Teflon filters, and the Teflon-quartz back-up filter is exposed to the ambient
23 concentration of organic vapors from the beginning of the sampling period. It might be expected
24 that the quantity of organic vapor adsorbed on quartz filters would depend on the organic
25 composition and would vary by season and location. However, it is also possible that the quartz
26 possesses a limited number of adsorption sites which are rapidly occupied so that the quantity of
27 OC on the back up filter would be relatively constant and depend on the pretreatment of the
28 quartz.

1 *Combined Measurement of Semivolatile Nitrate and OC and Nonvolatile Species (OC, EC,*
2 *Nitrate, and Sulfate)*

3 Fine particles in urban atmospheres contain substantial quantities of semivolatile material
4 (e.g., NH_4NO_3 and semivolatile organic compounds [SVOC]) that are lost from particles during
5 collection on a filter. Several diffusion denuder samplers have been developed for the
6 determination of both NO_3^- and organic semivolatile fine particulate components as well as
7 nonvolatile nitrate and organic compounds and nonvolatile sulfate (Pang et al., 2001; Eatough
8 et al., 1993). The combination of technology used in the BOSS diffusion denuder sampler and
9 the Harvard particle concentrator has resulted in the Particle Concentrator-Brigham Young
10 University Organic Sampling System (PC-BOSS) for the 24-hr integrated collection of $\text{PM}_{2.5}$,
11 including NH_4NO_3 and semivolatile organic material. Modifications of the BOSS sampler allow
12 for the determination of these same species on a time scale from a few hours to weekly (Ding et
13 al., 2002; Eatough et al., 1999a,b; 2001). Episodic studies have been conducted in Riverside,
14 CA and Bakersfield, CA (Obeidi et al., 2002) and Provo, UT (Obeidi and Eatough, 2002). The
15 average concentration of semivolatile and nonvolatile components in the three cities, during the
16 study periods, are shown in Figure 2-19.

17
18 **2.2.3.3 Continuous Measurement of Semivolatile and Nonvolatile Mass**

19 Techniques for the continuous measurement of PM mass is needed both to provide
20 real-time information on pollution levels (Long et al., 2002) and to reduce the costs involved in
21 visiting sites to change filters and in the equilibration and weighing of filters. Two techniques
22 are currently in use for the continuous measurement of PM mass. The TEOM is normally
23 operated at 50° C in order to remove particle-bound water. However, at 50° C most semivolatile
24 material is also evaporated. Therefore, the TEOM, operated at 50° C, may be considered to
25 measure the mass of nonvolatile PM. The beta gauge mass monitor changes the filter more
26 frequently than the TEOM and is less sensitive to changes in mass caused by changes in relative
27 humidity. It does not control the temperature at the filter. However, most beta gauge monitors
28 heat the inlet. This heating causes evaporation of a substantial fraction of the particle-bound
29 water and an unknown fraction of the semivolatile PM. Thus, the beta gauge may be considered
30 to measure the nonvolatile PM plus a small fraction of the particle-bound water and an unknown
31 fraction of the semivolatile PM. Three new techniques have been developed to address the issue
32 of lost semivolatile PM mass.

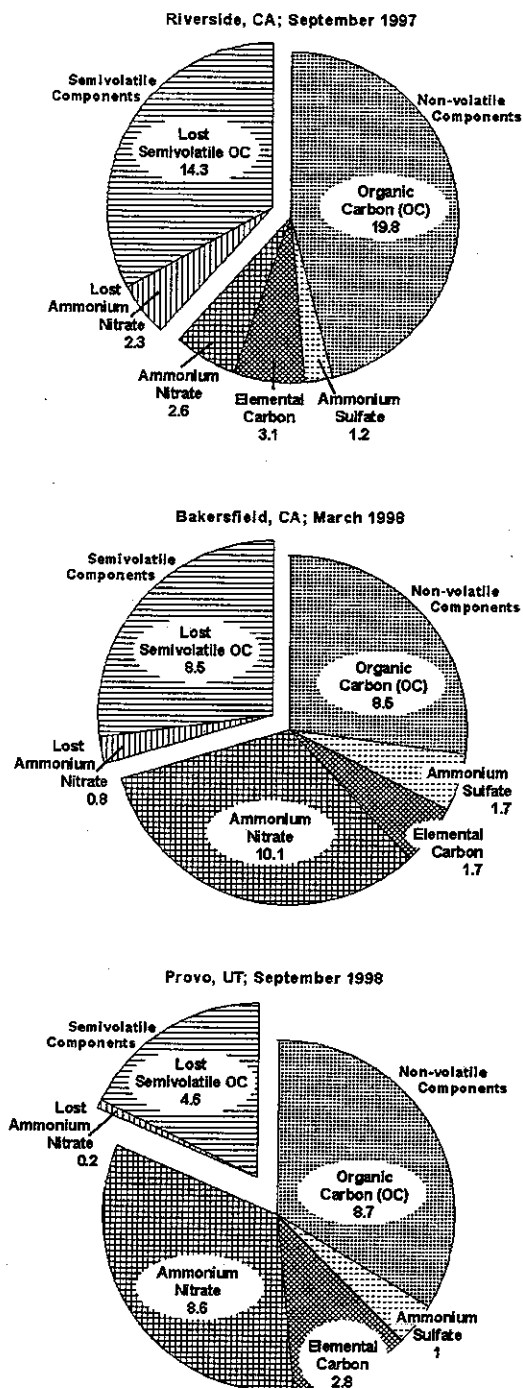


Figure 2-19. Average concentration of nonvolatile and semivolatile PM components in three cities ($\mu\text{g}/\text{m}^3$).

Source: Obeidi and Eatough (2002); Obeidi et al. (2002).

Real-Time Total Ambient Mass Sampler (RAMS)

The RAMS, a monitor based on diffusion denuder and TEOM monitor technology, has been developed, validated, and field tested for the real-time determination of total fine PM mass, including semivolatile PM (Eatough et al., 1999a; Obeidi and Eatough, 2002; Obedi et al., 2002; Pang et al., 2001). The RAMS measures the total mass of collected particles including semivolatile species with a TEOM monitor using a "sandwich filter." The sandwich contains a Teflon coated particle collection filter followed by a charcoal-impregnated filter (CIF) to collect any semivolatile species lost from the particles during sampling. Because the instrument measures total mass collected by the sandwich filter, all gas phase compounds that can be adsorbed by a CIF must be removed from the sampling stream prior to the TEOM monitor. Laboratory and field validation data indicate that the precision of fine PM mass determination is better than 10%. The RAMS uses a Nafion dryer to remove particle-bound water from the suspended particles and a particle concentrator to reduce the amount of gas phase organics that must be removed by the denuder. An example of data from the RAMS, the TEOM, and the PC-BOSS is shown in Figure 2-20. This figure also shows the PM_{2.5} mass from the TEOM as being negative for the hours of 16 to 19. This likely results from the loss of volatile materials from the heated filter.

Differential TEOM

Patashnick et al. (2001) developed a differential TEOM system that is based on a pair of TEOM sensors, each of which is preceded by its own electrostatic precipitator (ESP) and downstream from a common size selective inlet. By alternately switching the ESPs on and off and out of phase with each other, the two sensors measure "effective mass" that includes both the nonvolatile component and the volatile component sampled by the TEOM, less the volatile component that vaporized during the sampling interval. On the sensor side with the ESP turned on, there is no particle collection on that filter so that only volatilization of previously collected particles continues. This allows a correction for the effective mass as measured by the first sensor by subtracting out the volatilization artifact and leaving the nonvolatile and volatile components of the particulate matter. This system has yet to be well characterized for other biases or interferences such as reactions on the filters, particle collection efficiency of the ESPs, and particle and semivolatile material losses.

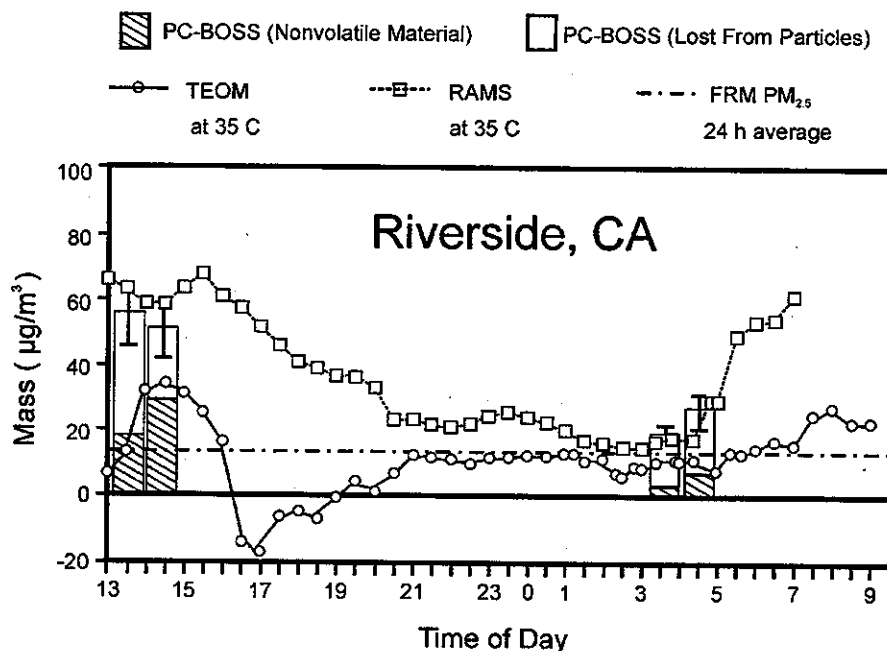


Figure 2-20. Comparison of mass measurements with colocated RAMS (real-time data), PC-BOSS (1-h data), FRM PM_{2.5} sampler (average of 24-h data), and a conventional TEOM monitor (real-time data). The semivolatile fine particulate matter is sampled with the RAMS and PC-BOSS, but not with the TEOM monitor or the FRM PM_{2.5} single filter sampler. The PC-BOSS provides information on both the nonvolatile component (NV) and the semivolatile organic component (SVOC).

Source: Eatough et al. (1999a).

1 **Continuous Ambient Mass Monitor (Camm)**

2 Koutrakis and colleagues (Koutrakis et al., 1996; Wang, 1997) have developed Camm, a
 3 technique for the continuous measurement of ambient particulate matter mass concentration
 4 based on the measurement of pressure drop increase with particle loading across a membrane
 5 filter. Recently, Sioutas et al. (1999) examined the increase in pressure drop with increasing
 6 particle loading on Nuclepore filters. They tested filters with two pore diameters (2 and 5 µm)
 7 and filter face velocities ranging from 4 to 52 cm s⁻¹ and examined the effects of relative
 8 humidity in the range of 10 to 50%. They found that, for hygroscopic ammonium sulfate
 9 particles, the change in pressure drop per unit time and concentration was a strong function of

1 relative humidity, decreasing with increasing relative humidity. These results suggest that
2 particulate concentration measurements, similar to the method of Koutrakis et al. (1996) that
3 uses the pressure drop method, may be subject to additional uncertainties if used in an
4 environment where the ambient relative humidity is quite variable and the relative humidity
5 where the particles are measured cannot be controlled accurately. The current version of the
6 CAMM (Wang, 1997) uses a particle concentrator, a Nafion dryer, and frequently moves the
7 filter tape to avoid artifacts due to evaporation of semivolatile components from the active
8 portion of the filter tape which would occur if the atmospheric concentration of the semivolatile
9 components decreased.

10 The CAMM was recently operated alongside a gravimetric PM method (the Harvard
11 Impactor, or HI) in seven U.S. cities selected for their distinctly different ambient particulate
12 compositions and densities. The correlation between the two methods was high, with an overall
13 r^2 of 0.90 and average CAMM/HI ratio of 1.07 (Babich et al., 2000).

14 15 **2.2.4 U. S. Environmental Protection Agency Monitoring Methods**

16 **2.2.4.1 The Federal Reference Methods for Measurement of Equilibrated Mass for PM₁₀,** 17 **PM_{2.5}, and PM_{10-2.5}**

18 In 1997, EPA promulgated new standards for PM_{2.5} to address fine-fraction thoracic
19 particles and retained with minor revisions the 1987 PM₁₀ standards to continue to address
20 coarse-fraction thoracic particles (Federal Register, 1997). In partial response to numerous
21 challenges to these standards, the U.S. Court of Appeals for the District of Columbia Circuit in
22 *American Trucking Association v. EPA*, 175 F. 3d 1027 (U.S. Court of Appeals, D.C. Cir. 1999)
23 found "ample support" for regulating coarse-fraction particles but revoked the revised PM₁₀
24 standards (leaving in effect the 1987 PM₁₀ standards) on the basis of PM₁₀ being a "poorly
25 matched indicator for coarse particulate pollution" because PM₁₀ includes fine particles.
26 Consistent with this specific aspect of the Court's ruling, which EPA did not appeal, EPA is now
27 considering use of PM_{10-2.5} as the indicator for coarse-fraction thoracic particles, in conjunction
28 with PM_{2.5} standards that address fine-fraction thoracic particles. Thus, EPA is now developing
29 a Federal Reference Method for the measurement of PM_{10-2.5}.

2.2.4.1.1 PM_{10}

The FRM specified for measuring PM_{10} (Code of Federal Regulations, 2001a,b) has been discussed in previous PM AQCD's and will only be mentioned briefly. The PM_{10} FRM defines performance specifications for samplers in which particles are inertially separated with a penetration efficiency of 50% at an aerodynamic diameter (D_a) of $10 \pm 0.5 \mu m$. The collection efficiency increases to $\approx 100\%$ for smaller particles and drops to $\approx 0\%$ for larger particles. Particles are collected on filters and mass concentrations are determined gravimetrically. Instrument manufacturers are required to demonstrate through field tests a measurement precision for 24-h samples of $\pm 5 \mu g/m^3$ for PM_{10} concentrations below $80 \mu g/m^3$ and 7% above this value. A number of samplers have been designated as PM_{10} reference samplers. The TEOM and several beta gauge samplers with 1-h time resolution have been designated as automated equivalent methods (U.S. Environmental Protection Agency, 2001).

2.2.4.1.2 $PM_{2.5}$

In contrast to the performance-based FRM standard for PM_{10} , the FRM for $PM_{2.5}$ (Code of Federal Regulations, 2001a) specifies certain details of the sampler design, as well as of sample handling and analysis, whereas other aspects have performance specifications (Noble et al., 2001). The $PM_{2.5}$ FRM sampler consists of a PM_{10} inlet/impactor, a $PM_{2.5}$ impactor with an oil-soaked impaction substrate to remove particles larger than $2.5 \mu m D_a$, and a 47-mm PTFE filter with a particle collection efficiency greater than 99.7%. The sample duration is 24 h, during which time the sample temperature is not to exceed ambient temperatures by more than $5^\circ C$. A schematic diagram of the $PM_{2.5}$ FRM sample collection system is shown in Figure 2-21. After collection, samples are equilibrated for 24 h at temperatures in the range of 20 to $23^\circ C (\pm 2^\circ C)$ and at relative humidities in the range of 30 to 40% ($\pm 5\%$). The equilibration tends to reduce particle-bound water and stabilizes the filter plus sample weight. Filters are weighed before and after sampling under the same temperature and relative humidity conditions. For sampling conducted at ambient relative humidity less than 30%, mass measurements at relative humidities down to 20% are permissible (Code of Federal Regulations, 2001a).

The PM_{10} inlet specified for the $PM_{2.5}$ FRM is modified from a previous low flow-rate PM_{10} inlet that was acceptable in both EPA-designated reference and equivalent PM_{10} methods. The modification corrects a flaw that was reported for the previous sampler, in that under some

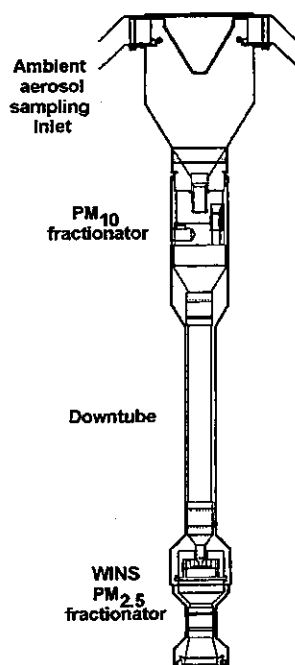


Figure 2-21. Schematic diagram of the sample collection portion of the PM_{2.5} FRM sampler.

Source: Noble et al. (2001).

1 meteorological conditions, the inlet may allow precipitation to penetrate the inlet. The
 2 modification includes a larger drain hole, a one-piece top plate, and louvers. Tolocka et al.
 3 (2001a) evaluated the performance of this modified inlet in a series of wind tunnel experiments.
 4 The modified inlet was found to provide a size cut comparable to the original inlet, for both
 5 PM_{2.5} and PM₁₀ sampling. Since the modification did not change the characteristics of the size
 6 cut, the modified inlet may be substituted for the original inlet as part of a reference or
 7 equivalent method for PM₁₀ and PM_{2.5} (Tolocka et al., 2001a).

8
 9 **WINS Impactor.** Design and calibration of the EPA PM_{2.5} Well Impactor Ninety-Six
 10 (WINS) is given by Peters et al. (2001a). The WINS impactor was designed to be deployed
 11 downstream of the Graseby-Andersen 246B PM₁₀ inlet as part of a sampler operating at a flow
 12 rate of 16.7 L/m. The WINS is pictured in Figure 2-22. The PM_{2.5} inlet consists of a single jet,
 13 directed toward a round hole, with a jet exit impaction surface comprised of a 37 mm diameter

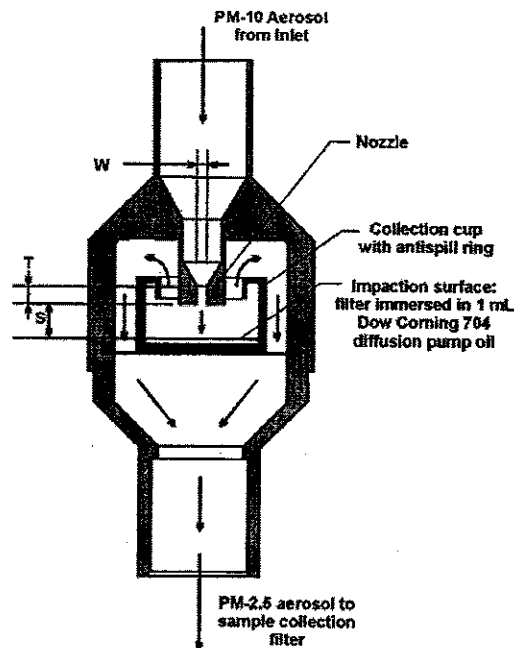


Figure 2-22. Schematic view of the final design of the WINS.

Source: Peters et al. (2001a).

glass fiber filter immersed in 1 ml of low volatility diffusion pump oil (i.e., the well). Particles not having enough inertia to be removed by the impactor are captured downstream on the sample collection filter. This design was selected to minimize impactor overloading that would otherwise result in particle bounce. The oil wicks through the particulate deposit on the impactor to provide a continuously wetted surface for impaction. The penetration curve indicated a 50% cutpoint of $2.48 \mu\text{m } D_a$ with a geometric standard deviation of 1.18 (Figure 2-23).

The WINS separator was evaluated for its loading characteristics (Vanderpool et al., 2001) by monitoring the performance after repeated operation in an artificially generated, high concentration, coarse-mode aerosol composed of Arizona Test Dust, as well as in the field in Rubidoux, Phoenix, Philadelphia, Research Triangle Park, and Atlanta. In the wind tunnel experiments, the WINS performance was found to be a monotonic function of loading. A minus 5% bias in the $\text{PM}_{2.5}$ measurement resulted from a coarse particulate loading of approximately 16 mg. This negative bias was due to a slight reduction in the separator cutpoint. It was also

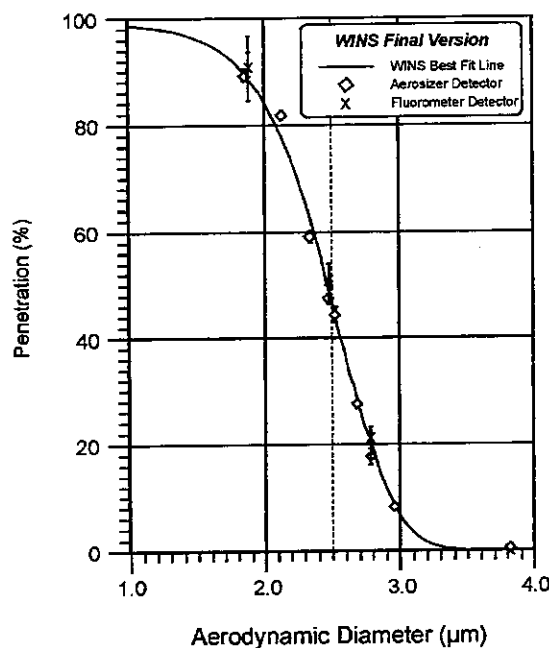


Figure 2-23. Evaluation of the final version of the WINS.

Source: Peters et al. (2001a).

found that the predictable results from the controlled laboratory experiments could not be extrapolated to field settings and that the WINS performance was more sensitive to the impactor loading in the field than it was in experiments with the single component aerosol. Significant particle bounce was not observed in either the laboratory or the field experiments. Vanderpool et al. (2001) concluded that their study supports the recommendation that the FRM WINS wells should be replaced after every 5 days of 24-h operation (U.S. Environmental Protection Agency, 1998).

A detailed sensitivity study of the WINS impactor was conducted (Vanderpool et al., 2001) in which the effects on the impactor performance of a number of parameters were examined. The results of this study are summarized in Table 2-3.

The regulations also allow for Class I, II, and III equivalent methods for $PM_{2.5}$ (Code of Federal Regulations, 2001c). Class I equivalent methods use samplers with relatively small deviations from the sampler described in the FRM. Class II equivalent methods include “all other $PM_{2.5}$ methods that are based upon 24-h integrated filter samplers that are subjected to

TABLE 2-3. SUMMARY OF SENSITIVITY STUDIES OF WINS IMPACTOR PERFORMANCE

Parameter	Amount of variance	Cutpoint variation	PM _{2.5} mass concentration bias
Manufacturing tolerances on WINS components	Specified tolerances	0.05 micrometers	<1%
Flow control biases	4%	0.05 micrometers	Cutpoint shift partially offset volume bias
T and P measurement	Allowable ambient	± 0.02 micrometers	± 0.4%
Diffusion oil volume	0.75 ml to 3 ml	No effect	
Impactor loading	After 5 24 h events	-0.07 micrometers	<1.5%
Ambient P variations		Negligible	Negligible
Air Properties	0 C	2.40 micrometers	NA
Impactor oil crystallization		No effect	No effect
Impactor oil viscosity	-20 C	No effect	No effect
	-35 C	Need to change WINS more frequently than every 5 days	

Source: Vanderpool et al. (2001).

subsequent moisture equilibration and gravimetric mass analysis.” Class III equivalent methods include non-filter-based methods such as beta attenuation, harmonic oscillating elements, or nephelometry (McMurry, 2000). As of July 2001, 11 PM_{2.5} samplers (listed in Table 2-4) had been tested and led to the conclusion that the PM₁₀ sampling systems can be designed such that concentration measurements are precise to ± 10%. For PM_{2.5}, cutpoint tolerances are not expected to affect the mass concentration as much as for PM₁₀, because the 2.5 µm D_a cutpoint generally occurs near a minimum in the mass distribution (e.g., Figure 2-5).

The PM_{2.5} mass concentration will be affected, on the other hand, by other sampling issues mentioned but not discussed extensively in the previous 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a). These issues have been discussed earlier in this chapter and include gas/particle, particle/particle, and particle/substrate interactions for sulfates and nitrates (e.g., Appel et al., 1984), volatilization losses of nitrates (Zhang and McMurry, 1992), semivolatile organic compound artifacts (e.g., Eatough et al., 1993), and relative humidity effects (e.g., Keeler et al., 1988).

**TABLE 2-4. PM_{2.5} SAMPLERS CURRENTLY DESIGNATED AS FRMs FOR
PM_{2.5} MASS CONCENTRATIONS**

Sampler	Manufacturer	Description	Federal Register Reference
RAAS2.5-100	Andersen Instruments	FRM single	Vol. 63, p. 31991, 6/11/98
RAAS2.5-300	Andersen Instruments	FRM sequential	Vol. 63, p. 31991, 6/11/98
RAAS2.5-200	Andersen Instruments	FRM audit	Vol. 64, p. 12167, 3/11/99
Partisol 2000	Rupprecht & Patashnick	FRM single	Vol. 63, p. 18911, 4/16/98
Partisol-Plus 2025	Rupprecht & Patashnick	FRM sequential	Vol. 63, p. 18911, 4/16/98
Partisol 2000 audit	Rupprecht & Patashnick	FRM audit	Vol. 64, p. 19153, 4/19/99
PQ 200	BGI, Inc.	FRM single	Vol. 63, p. 18911, 4/16/98
PQ 200A	BGI, Inc.	FRM audit	Vol. 63, p. 18911, 4/16/98
605 CAPS	ThermoEnvironmental Instruments	FRM single	Vol. 63, p. 58036, 10/29/98
MASS 100	URC	FRM single	Vol. 65, p. 26603, 05/08/00
MASS 300	URC	FRM sequential	Vol. 65, p. 26603, 05/08/00

Source: Peters et al. (2001b); U.S. Environmental Protection Agency (2001).

Several studies now have been reported in which the FRM was collocated with other PM_{2.5} samplers in intercomparison studies. During the Aerosol Research and Inhalation Epidemiology Study (ARIES), several PM_{2.5} samplers were collocated at a mixed industrial-residential site near Atlanta, GA (Van Loy et al., 2000). These samplers included a standard PM_{2.5} FRM, a TEOM with Nafion drier, a particulate composition monitor (PCM; Atmospheric Research and Analysis, Cary, NC), a medium-volume (113 L/min flow rate) fine particle (PM_{2.5}) and semivolatile organic compound (i.e., a filter followed by a solid adsorbent) sampler, operated by the Desert Research Institute, a HEADS sampler, and a dichotomous sampler for coarse PM. The PCM sampler has three channels, all of which have PM₁₀ cyclone inlets. The first two channels both have two denuders preceding a 2.5-μm WINS impactor and filter packs. The first denuder is coated with sodium carbonate to remove acid gases, and the second is coated with citric acid to remove ammonia. The third channel has a carbon coated parallel-plate denuder preceding the WINS impactor. Measurements of 24-h mass from the FRM, PCM, and TEOM samplers, as well as reconstructed PM_{2.5} mass (RPM), were compared for a 12-mo period. The slopes for the TEOM-FRM, PCM-FRM, and RPM-FRM correlations were 1.01, 0.94, and 0.91,

1 respectively; whereas the y-intercepts for each were 0.68, 0.04, and 0.98. Particulate sulfate
2 measurements on the FRM Teflon filter, the PCM Teflon filter, and PCM Nylon filter were
3 nearly identical. Nitrate results from the three filters were much less consistent, with the FRM
4 collecting substantially less nitrate than that collected on either the denuded nylon filter or a
5 denuder followed by a Teflon-nylon filter sandwich. Particulate ammonia measurements were
6 also compared and showed more scatter than the sulfate measurements but less than the nitrate
7 measurements.

8 An intercomparison of both PM_{10} and $PM_{2.5}$ mass measurements was conducted during the
9 1998 Baltimore PM Study (Williams et al., 2000). PM monitors were collocated at a residential
10 indoor, residential outdoor, and ambient monitoring site within Baltimore County, MD. PM
11 samplers included TEOMs, $PM_{2.5}$ FRMs, cyclone-based inlets manufactured by University
12 Research Glassware (URG), and Versatile Air Pollution Samplers (VAPS). The VAPS sampler
13 is a dichotomous sampler operating at 33 L/min (one coarse particle channel at 3 L/min, and two
14 fine particle channels at 15 L/min, each). In the configuration employed during this study, one
15 fine particle channel was operated with a Teflon filter backed by a nylon filter and preceded by a
16 sodium carbonate coated annular denuder; the second fine particle channel had a quartz filter
17 preceded by a citric acid-coated annular denuder; and the coarse particle channel had a
18 polycarbonate filter followed by a Zefluor filter for flow distribution. Differences in $PM_{2.5}$ mass
19 concentrations between the samplers, although not large, were attributed to potential particle
20 nitrate losses, denuder losses, and losses of SVOC for some samplers. Differences between
21 coarse particulate mass concentrations, on the other hand, varied widely between the
22 instruments.

23 In another intercomparison study, Tolocka et al. (2001b) examined the magnitude of
24 potential sampling artifacts associated with the use of the FRM by collocating FRMs alongside
25 other chemical speciation samplers at four U.S. cities. The locations included a high nitrate and
26 carbon, low sulfate site (Rubidoux, CA); high crustal, moderate carbon and nitrate site
27 (Phoenix); high sulfate, moderate carbon, and low nitrate (Philadelphia); and low $PM_{2.5}$ mass
28 (Research Triangle Park, NC). The use of Teflon and heat-treated quartz filters was also
29 examined in this study. The Teflon filters collected less nitrate than the heat-treated quartz
30 filters. Filters in samplers using denuders to remove organic gases collected less organic PM
31 than filters in samplers without denuders.

Peters et al. (2001b) compiled the results of several field studies in which a number of FRM and other $PM_{2.5}$ samplers were intercompared. In addition to the FRM samplers listed in Table 2-3, other $PM_{2.5}$ samplers included the Sierra Instruments dichotomous sampler, the Harvard impactor, the IMPROVE sampler, and the Air Metrics saturation monitor. Results were compiled from $PM_{2.5}$ field studies conducted in Birmingham, Denver, Bakersfield, Phoenix, Research Triangle Park, Atlanta, and Rubidoux. Limited studies on precision for the non-FRM samplers suggest that the Harvard Impactor and dichotomous samplers had the lowest coefficient of variations (CV), with both under 10%. The CV for this study was calculated by dividing the sample standard deviation by the average concentration. The IMPROVE samplers had CVs between 10 and 12%, and the Air Metrics samplers had the highest observed CVs, over 15%. In intercomparisons with FRM samplers, the non-FRM samplers showed strong linear relationships in comparison to the FRM sampler; however, none of the comparisons passed the current EPA Subpart C equivalent method criteria, which EPA is in the process of revising.

Detailed information on precision of PM samplers used in monitoring networks may be found in EPA's Technology Transfer Network website (U.S. Environmental Protection Agency, 2002a).

2.2.4.1.3 $PM_{10-2.5}$

Measurement techniques for $PM_{10-2.5}$ are somewhat more complex than those for $PM_{2.5}$ or PM_{10} because, for $PM_{10-2.5}$, it is necessary to isolate a size fraction between an upper 50% cut point of $10 \mu m D_a$ and a lower 50% cut point of $2.5 \mu m D_a$. EPA is currently developing an FRM for $PM_{10-2.5}$. Several candidate techniques are discussed below.

The Difference Method. One approach to measurement of $PM_{10-2.5}$ is to make separate measurements of PM_{10} and $PM_{2.5}$ and take the difference of the resulting equilibrated masses. One problem is that, if either the $PM_{2.5}$ or the PM_{10} sampler fails, no $PM_{10-2.5}$ measurement can be obtained. In addition, errors in cut-point, flow rate, and filter weights (both before use and after collection and equilibration of particles) and uncertainties due to loss of semivolatile components of PM may occur for each size cut. Careful control of flow rate and equivalent treatment of PM_{10} and $PM_{2.5}$ filters in terms of pressure drop across the filter and temperature of the filter during and after collection can improve precision and accuracy. Allen et al. (1999a)

1 summarized several sampling issues to consider in measuring coarse particulate mass by
2 difference, including the use of identical instrumentation (except cutpoints), filter media, filter
3 face velocity, and ambient-filter temperature differences; common flow measurement devices;
4 use of higher sampler flow rates (10 L/min minimum for 24-h sample is recommended); and
5 avoiding excessive filter loading. The concern, expressed by Allen et al. (1999a), that the “pie-
6 plate” inlet required by the final version of the PM_{2.5} FRM might have a different cut point than
7 the “flat-top” inlet of the PM₁₀ FRM, has been addressed by a wind tunnel study which found
8 both to have an appropriate PM₁₀ cut point (Tolocka et al., 2001a).

9 Since the difference method requires weighing two filters, the key to obtaining high
10 precision in the coarse mass measurement is precise measurements of filter weights. Allen et al.
11 (1999a) discuss techniques for increasing the precision of the difference method by reducing
12 errors in filter weights. These include proper temperature and humidity controls, use of a high
13 quality microbalance, 100% replicate weighings, control of static charge, aging of new filters,
14 weighing of a sufficient number of laboratory blank filters, and accounting for buoyancy errors
15 caused by variability in barometric pressure. Allen et al. (1999a) emphasize the necessity of
16 replicate weighing of filters and a third weighing if the difference between the first two weights
17 exceeds a specified minimum. Lawless et al. (2001) investigated the magnitude of uncertainties
18 attributed to fluctuations in some of these parameters (humidity, temperature, drafts, vibration,
19 and electrostatic charges) and recommended methods for improving their control. Koistinen
20 et al. (1999) and Hänninen et al. (2002) give an excellent discussion of the procedures developed
21 to overcome problems associated with gravimetric measurements of PM_{2.5} mass in the EXPOLIS
22 (The Air Pollution Exposure Distributions Within Adult Urban Populations in Europe) Study.
23 They discuss factors such as corrections for buoyancy, elimination of static charge, and increases
24 in the mass of blank filters with time. The establishment of a temperature and humidity
25 controlled room required for the equilibration and weighing of filters for the FRM is expensive.
26 Allen et al. (2001) describe a more cost-effective technique that uses a chamber with relative
27 humidity controlled at 34% relative humidity by a saturated aqueous solution of MgCl₂.

28 Allen et al. (1999a) recommend that, in reporting precision from collocated samplers both
29 the (CV) and the square of the correlation coefficient (r^2) be reported. For a study in Boston with
30 27 pairs of mass data from collocated PM₁₀ and PM_{2.5} using standard weighing methods, they
31 obtained a CV of 4.7% and an r^2 of 0.991 for PM_{2.5}, a CV of 4.4% and an r^2 of 0.994 for PM₁₀.

1 and a CV of 15% and an r^2 of 0.88 for $PM_{10-2.5}$. By using duplicate weighings and other
2 techniques suggested for improving precision, they obtained a CV of 1.3% and an r^2 of 0.998 for
3 $PM_{2.5}$ in a study in Chicago with 38 collocated measurements. On the basis of the improvement
4 in the CV for $PM_{2.5}$, they estimate that use of the recommended techniques for $PM_{10-2.5}$ by
5 difference would have yielded a CV of 3.8% and an r^2 of 0.98 if they had been applied in the
6 Chicago study.

7
8 **Multistage Impaction.** A second technique involves the use of impaction to isolate the
9 size fraction between 2.5 and 10 $\mu m D_a$. In the impaction process, the air stream is first
10 accelerated through a small hole (nozzle) or slit. The air stream is directed so that it "impacts"
11 on a surface. Depending on the velocity and pressure of the air stream, particles smaller than a
12 certain size will follow the air stream around the impactor surface. Larger particles will impact
13 on the surface. In practice, impactors have 50% cut points similar to those for the rejection of
14 larger particles in $PM_{2.5}$ and PM_{10} samples (see Figure 2-6).

15 Multistage impactors are used to separate particles into several size fractions for the
16 determination of mass and chemical composition as a function of size (Wang and John, 1988;
17 Marple et al., 1991). The major problem with the use of impactors to separate the 10-2.5 $\mu m D_a$
18 fraction of coarse particles (thoracic coarse PM) is bounce. Coarse particles tend to be dry, solid
19 particles. When they hit a hard surface, they can bounce and be carried away with the air stream
20 (e.g., Dzuby et al., 1976; Wesolowski et al., 1977; Rao and Whitby, 1978; Cheng and Yeh,
21 1979; Wang and John, 1987; John and Sethi, 1993). Various techniques have been used to
22 reduce bounce. One technique is to use a porous substance such as a glass or quartz fiber filter
23 (Chang et al., 1999) material or a polyurethane foam (Breum, 2000; Kavouras and Koutrakis,
24 2001). These techniques may result in less precise separation and yield a sample that must be
25 extracted before chemical analyses can be performed. Another technique is to coat the impactor
26 with a soft wax or grease (Rao and Whitby, 1977; Turner and Hering, 1987; Pak et al., 1992).
27 This can cause problems with weighing and chemical analyses. In addition, as the deposit of
28 particles builds up, incoming particles may not hit the soft surface, but instead hit a previously
29 collected hard particle and bounce off of it. The WINS impactor discussed earlier uses a filter in
30 a well of low volatility oil to ensure a wetted surface at all times. However, such a technique,

1 while appropriate for removing unwanted particles, would not yield a particle sample suitable for
2 weighing or for chemical analyses.

3
4 *Virtual Impaction.* The problems of bounce and blow off of particles from impactors,
5 especially for the collection of large quantities of particles, was addressed by aerosol scientists in
6 the mid-1960s by the development of what is now known as "virtual" impaction (Hounam and
7 Sherwood, 1965; Conner, 1966).

8 In a virtual impactor, a hole is placed in the impaction plate just below the accelerating jet.
9 Two controlled flows allow a fraction, e.g., 10% (or another predetermined fraction, typically 5 -
10 20%), of the air containing the coarse particles to go through the hole and through a filter (minor
11 flow). A 10% minor flow gives a coarse channel enrichment factor of 10. The remaining
12 fraction (e.g., 90% of the airflow) containing the fine particles follows a different path and goes
13 through a second filter (major flow). The upper cutpoint is usually set by the inlet (e.g.,
14 10 μm D_p). The flow rates, pressures, and distance from the nozzle to the virtual impactor
15 surface can be varied to direct particles with an D_p greater than the lower cutpoint (i.e.,
16 $> 2.5 \mu\text{m}$) to go through the hole and be collected on the first filter and to direct smaller particles
17 (i.e., $< 2.5 \mu\text{m}$) to flow around the impactor be collected on the second filter. Large particles
18 "impact" into the hole with a small amount of the air flow. The smaller particles follow the
19 major air flow around the impactor plate. This technique overcomes the problem of bounce.
20 An example of the separation into fine and coarse particles is shown in Figure 2-24.

21 The usefulness of this technique for collecting samples of fine and coarse particles for
22 chemical analysis was recognized by EPA in the mid-1970s. A development program was
23 undertaken leading to the development of the now well known "dichotomous sampler" (a virtual
24 impactor that separates particles into two size fractions) and an associated XRF analyzer
25 (Dzubay and Stevens, 1975; Loo et al., 1976; Jaklevic et al., 1977; Dzubay et al., 1977). The
26 dichotomous sampler was originally developed for use in the Regional Air Monitoring Study
27 (RAMS), part of the Regional Air Pollution Study (RAPS), conducted in St. Louis, Missouri in
28 the mid-1970s. Dichotomous samplers were operated at 10 RAMS sites from March 1975 to
29 March 1977; and 33,695 filters were collected and analyzed by XRF with an overall sampling
30 efficiency of 97.25% (Strothmann and Schiermeier, 1979; Loo et al., 1976; Loo et al., 1978;
31 Dzubay, 1980; Lewis and Macias, 1980). Dichotomous samplers were a novel concept at that

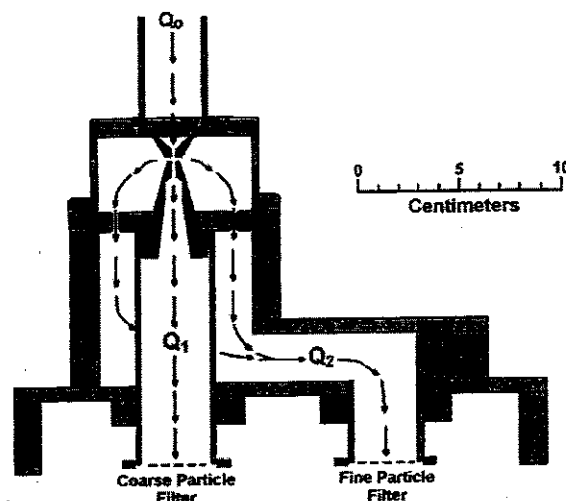


Figure 2-24. Schematic diagram showing the principle of virtual impaction. The initial flow, Q_0 , is split into a minor flow, Q_1 , which carries the larger particles, which impact into the hole, to the coarse particle filter and a major flow, Q_2 , which carries the smaller particles, which can follow the airflow, to the fine particle filter.

Source: Loo et al. (1976).

time. Concern over particle losses and other problems at cut point sizes smaller than $2.5 \mu\text{m } D_a$ influenced the decision to choose 2.5 instead of 1.0 as the cut point diameter.

Subsequent to the use of the dichotomous sampler in RAPS, considerable progress has been made in the theory and practice of designing virtual impactors, especially in how to reduce losses and provide a sharp cut (Masuda et al., 1979; Marple and Chien, 1980; Chen et al., 1985, 1986; Loo and Cork, 1988). Now virtual impactors, with rectangular slits or round holes, are used (a) to provide cut point sizes as low as $0.15 \mu\text{m } D_a$ and (b) to concentrate coarse, accumulation, and ultrafine mode particles for use in health studies (Solomon et al., 1983; Marple et al., 1990; Sioutas et al., 1994a,b,c). Dichotomous samplers were also used in a national network to measure $\text{PM}_{2.5}$ and $\text{PM}_{10-2.5}$ in the Harvard Six City Study (Spengler and Thurston, 1983; Dockery et al., 1993) and the Inhalable Particulate Network (Suggs and Burton, 1983). A trichotomous high volume sampler has also been developed that provides samples of particles less than $1.0 \mu\text{m}$, $1.0 \mu\text{m} - 2.5 \mu\text{m}$, and $2.5 \mu\text{m}$ (Marple and Olsen, 1995). This

sampler was intended for study of the composition of the intermodal mass between 1.0 and 2.5 μm D_g .

More recently, two dichotomous sequential PM air samplers were collocated with a manual Federal Reference Method (FRM) air sampler and operated for over one year at a waterfront site on Tampa Bay (Poor et al., 2002). The FRM sampler was alternately configured as a $\text{PM}_{2.5}$, then as a PM_{10} sampler. For the dichotomous sampler measurements, daily 24-h integrated $\text{PM}_{2.5}$ and $\text{PM}_{10-2.5}$ ambient air samples were collected at a total flow rate of 16.71 min^{-1} . As was the case in earlier versions of the dichotomous sampler, a virtual impactor split the air into flow rates of 1.67 and 15.01 min^{-1} and collected $\text{PM}_{10-2.5}$ and $\text{PM}_{2.5}$ on 47-mm diameter PTFE® filters. Between the two dichotomous air samplers, the average concentration, relative bias and relative precision for $\text{PM}_{2.5}$ were $13.3 \mu\text{g m}^{-3}$, 0.02% and 5.2% concentrations ($n = 282$), and for $\text{PM}_{10-2.5}$ were $12.3 \mu\text{g m}^{-3}$, 3.9% and 7.7% ($n = 282$). FRM measurements were alternate day 24-h integrated $\text{PM}_{2.5}$ or PM_{10} ambient air samples collected onto 47-mm diameter PTFE® filters at a flow rate of 16.71 min^{-1} . Between a dichotomous and a $\text{PM}_{2.5}$ FRM air sampler, the average concentration, relative bias and relative precision were $12.4 \mu\text{g m}^{-3}$, -5.6% and 8.2% ($n = 43$); and between a dichotomous and a PM_{10} FRM air sampler, the average concentration, relative bias and relative precision were $25.7 \mu\text{g m}^{-3}$, -4.0% and 5.8% ($n = 102$). The $\text{PM}_{2.5}$ concentration measurement standard errors for two dichotomous and one FRM samplers were 0.95, 0.79 and $1.02 \mu\text{g m}^{-3}$; and for PM_{10} , the standard errors were 1.06, 1.59, and $1.70 \mu\text{g m}^{-3}$. The authors (Poor et al., 2002) concluded that their results indicate that "the dichotomous samplers have superior technical merit" and demonstrate "the potential for the dichotomous sequential air sampler to replace the combination of the $\text{PM}_{2.5}$ and PM_{10} FRM air samplers, offering the capability of making simultaneous, self-consistent determinations of these particulate matter fractions in a routine ambient monitoring mode."

The dichotomous sampler provides two separate samples. However, a fraction of the smaller particles, equal to the minor flow, will go through the virtual impaction opening with the air stream and be collected on the coarse particle filter. In the dichotomous sampler used in the RAPS program, 10% of the fine particles were collected with the coarse particles. Thus, in order to determine the mass or composition of the coarse particles, it is necessary to determine the mass and composition of the fine particles and subtract the appropriate fraction from the mass or composition of the particles collected on the coarse particle filter. Allen et al. (1999b) discuss

1 potential errors in the dichotomous sampler caused by uncertainties in the coarse mass channel
2 enrichment factor. Virtual impactors have also been designed with a clean air jet in the center of
3 the round nozzle. This makes possible lower contamination of coarse particles by fine particles
4 but maintains low losses and sharp cuts (Chen and Yeh, 1986; Chien and Lundgren, 1993). The
5 fine particle intrusion into the coarse particle sample can also be reduced by operating two
6 virtual impactors in series (Dzubay and Stevens, 1975).

7 Aerosol physicists have also conducted theoretical and experimental investigations of
8 virtual impaction using slits instead of round holes (Forney et al., 1978, 1982; Ravenhall et al.,
9 1978; Masuda and Nakasita, 1988; Sioutas et al., 1994b, c, d; Ding and Koutrakis, 2000). The
10 slit virtual impactor permits much higher flow rate than round hole virtual impactors and
11 resolves problems that occur with multihole virtual impactors (Marple et al., 1990; Fang et al.,
12 1991). The slit technique has been used to develop virtual impaction systems for concentrating
13 particles in the size range 0.1 to 2.5 μm D_p for exposure studies using animals and people
14 (Sioutas et al., 1995a, b). The slit impactor can also be used to concentrate coarse particles for
15 measurement (Misra et al., 2001) or exposure studies (Chang et al., 2002). It has also been
16 possible to concentrate ultrafine particles ($> 0.1 \mu\text{m}$) by first separating ultrafine particles from
17 larger particles, adding water vapor to saturate the air containing the ultrafine particles, cooling
18 the air to cause supersaturation and growth of the ultrafine particles into the 1.0 – 4.0 μm size
19 range, concentrating these particles with a slit virtual impactor, and heating the air to return the
20 particles to their original size (Sioutas and Koutrakis, 1996; Sioutas et al., 1999; Sioutas et al.,
21 2000; Kim et al., 2001b,c; Geller et al., 2002).

22 23 **2.2.5 Speciation Monitoring**

24 ***Speciation Network and Monitoring***

25 In addition to FRM sampling to determine compliance with PM standards, EPA requires
26 states to conduct chemical speciation sampling primarily to determine source categories and
27 trends (Code of Federal Regulations, 2001b). Source category apportionment calculations are
28 discussed in Chapter 3. A $\text{PM}_{2.5}$ chemical Speciation Trends Network (STN) has been deployed
29 that consists of 54 core National Ambient Monitoring Stations (NAMS) and approximately
30 250 State and Local Air Monitoring Stations (SLAMS). In addition, over 100 IMPROVE
31 (Interagency Monitoring of Protected Visual Environments) samplers located at regional

1 background and transport sites can be used to fulfill SLAMS requirements. The overall goal of
2 the speciation program is "to provide ambient data that support the Nation's air quality program
3 objectives" (U.S. Environmental Protection Agency, 1999). Information and reports on EPA's
4 speciation monitoring program may be found on EPA's Technology Transfer Network at
5 <http://www.epa.gov/ttn/amtic/pmspec.html>. The NAMS speciation sites will provide routine
6 chemical speciation data that will be used to develop annual and seasonal aerosol
7 characterization, air quality trends analysis, and emission control strategies. The SLAMS
8 speciation sites will further support the NAMS network and provide information for
9 development of State Implementation Plans (SIPs).

10 At both NAMS and SLAMS sites, aerosol samples will be collected for analysis of trace
11 elements, ions (sulfate, nitrate, ammonium, sodium, and potassium), and total carbon. The
12 NAMS speciation sites will operate on a 1 in 3 day schedule, with 10 of these sites augmented
13 with continuous speciation analyses for everyday operation. The SLAMS speciation sites will
14 generally operate on a 1 in 6 day basis; however, many sites may be operated on a 1 in 3 day
15 basis in locations where increased data collection is needed. There are several samplers that are
16 suitable for use in the NAMS/SLAMS network. These samplers include an inlet cutpoint with
17 size cut characteristics comparable to the WINS FRM; proven denuder technology for nitrate;
18 and sampler face velocity and sample volume similar to that of the FRM. The current samplers
19 include three filters: (1) Teflon for equilibrated mass and elemental analysis by energy
20 dispersive x-ray fluorescence (EDXRF), (2) a nitric acid denuded Nylon filter for ion analysis
21 (ion chromatography), (3) a quartz fiber filter for elemental and organic carbon. EC and OC are
22 determined by thermal optical analysis via a modification of the NIOSH (National Institute for
23 Occupational Safety and Health) method 5040 (Thermal Optical Transmission) [TOT]).
24 However, no corrections are made for positive artifacts caused by adsorption on organic gases or
25 the quartz filters or negative artifacts due to evaporation of semivolatile organic compounds
26 from the collected particles.

27 Since 1987, the IMPROVE network has provided measurements of ambient PM and
28 associated light extinction in order to quantify PM chemical components that affect visibility at
29 Federal Class 1 areas that include designated national parks, national monuments, and
30 wilderness areas. Management of this network is a cooperative effort between U.S. EPA, federal
31 land management agencies, and state governments. The IMPROVE program has established

1 protocols for analysis of aerosol measurements that provide ambient concentrations for PM₁₀,
2 PM_{2.5}, sulfates, nitrates, organic and elemental carbon, crustal material, and a number of other
3 elements. Information on the IMPROVE program may be found at
4 <http://vista.cira.colostate.edu/improve>.

5 IMPROVE aerosol monitoring consists of a combination of particle sampling and sample
6 analysis. The IMPROVE sampler, which collects two 24-hour duration samples per week,
7 simultaneously collects one sample of PM₁₀ on a Teflon filter, and three samples of PM_{2.5} on
8 Teflon, nylon, and quartz filters. PM₁₀ mass concentrations are determined gravimetrically from
9 the PM₁₀ filter sample, while PM_{2.5} mass concentrations are determined gravimetrically from the
10 PM_{2.5} Teflon filter sample. The PM_{2.5} Teflon filter sample is also used to determine
11 concentrations of selected elements using particle-induced x-ray emission (PIXE), x-ray
12 fluorescence (XRF), and Proton Elastic Scattering Analysis (PESA). The PM_{2.5} nylon filter
13 sample, which is preceded by a denuder to remove acidic gases, is analyzed to determine nitrate
14 and sulfate aerosol concentrations using Ion Chromatography (IC). Finally, the PM_{2.5} quartz
15 filter sample is analyzed for organic and elemental carbon using the Thermal Optical Reflectance
16 (TOR) method. Corrections are made for positive artifacts but not for negative artifacts.

17 The STN and the IMPROVE networks represent a major advance in the measurement of
18 nitrate since the combination of a denuder to remove nitric acid vapor and a Nylon filter to
19 adsorb nitric acid vapor that volatilizes from the collected ammonium nitrate particles
20 overcomes the loss of nitrate from Teflon filters. However, the different techniques used for the
21 measurement of OC and EC lead to significant differences between OC and EC measurements
22 when the two techniques are intercompared (Chow et al., 2001). IMPROVE yields higher EC
23 and lower OC although there is good agreement for TC. Another difference arises from the
24 treatment of the positive artifact due to the absorption of organic gases by the quartz filters used
25 in IMPROVE and STN samplers. More information on these differences is given in Section
26 2.2.7 and details are discussed in Appendix 2B.

27 Several of the PM_{2.5} size selectors developed for use in the EPA National PM_{2.5} STN were
28 recently evaluated by comparing their penetration curves under clean room experiments with
29 that of the WINS impactor (Peters et al., 2001c). The corresponding speciation monitors were
30 then compared to the FRM in four cities. The PM_{2.5} inlets tested were the SCC 2.141 cyclone
31 (6.7 L/min) that is in the Met One Instruments SASS sampler; the SCC 1.829 cyclone

(5.0 L/min) that is proposed for use in the Rupprecht and Patashnik real-time sulfate/nitrate monitor; the AN 3.68 cyclone (24.0 L/min) that is in the Andersen RAAS; and the spiral separator (7.0 L/min) that was previously in the Met One SASS. The cutpoints of the SCC cyclones compared reasonably well with the WINS (2.52 and 2.44 micrometers for the SCC 2.141 and SCC 1.829, respectively, at their design flowrates), but both demonstrated a tail extending into the coarse particle mode. The AN inlet had the sharpest cutpoint curve, but the 50% cutpoint diameter was $2.7 \mu\text{m D}_a$ at its design flowrate. The spiral inlet had the shallowest cutpoint curve, and the 50% cut point was 2.69 and $2.67 \mu\text{m D}_a$ for an ungreased and greased inlet, respectively. The speciation samplers were also compared to the FRM sampler with WINS inlet under ambient conditions in four cities. The Andersen RAAS equipped with the AN 3.68 cyclone compared well to the FRM in all four cities, when compared on the basis of $\text{PM}_{2.5}$ mass, sulfate, and crustal concentrations. Greasing the spiral inlet in the Met One sampler improved the performance of that sampler, which tended to give much higher $\text{PM}_{2.5}$ concentrations than the FRM in cities with high crustal particulate matter.

2.2.6 Inorganic Elemental Analyses

In addition to the lighter elements, hydrogen, carbon, oxygen and nitrogen, the following 40 heavier elements are commonly found in ambient air samples: sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, arsenic, selenium, bromine, rubidium, strontium, yttrium, zirconium, molybdenum, palladium, silver, cadmium, indium, tin, antimony, barium, lanthanum, gold, mercury, thallium, lead, and uranium. These often indicate air pollution sources and several of them are considered to be toxic (transition metals, water-soluble metals, and metals in certain valence states [e.g., Fe(II), Fe(III), Cr(III), Cr(VI), As(III), As(V)]). Measurement methods for inorganic elements are listed in Table 2-5. These methods differ with respect to detection limits, sample preparation, and cost (Chow, 1995). EDXRF and PIXE are the most commonly applied methods because they quantify more than 40 detectable elements, they are non-destructive, and they are relatively inexpensive. Both were discussed in the previous 1996 PM AQCD. TRXRF and S-XRF are newer techniques with lower detection limits. AAS, ICP-AES, and ICP-MS are also appropriate for ionic measurements of elements that can be dissolved. PESA provides a means for measuring

TABLE 2-5. MEASUREMENT METHODS FOR INORGANIC ELEMENTS

#	Acronym	Full Name	Comments
1.	EDXRF	energy dispersive x-ray fluorescence	heavier elements
2.	S-XRF	synchrotron induced X-ray emission	heavier elements; lower detection limits than EDXRF
3.	PIXE	proton induced x-ray emission	heavier elements; lower detection limits than EDXRF
4.	PESA	proton (or particle) elastic scattering analysis	lighter elements
5.	TRXRF	total reflection X-ray fluorescence	heavier elements; lower detection limits than EDXRF
6.	INAA	instrumental neutron activation analysis	many elements; sensitivity different than EDXRF
7.	AAS	atomic absorption spectrophotometry	many elements that can be dissolved
8.	ICP-AES	inductively coupled plasma with atomic emission spectroscopy	many elements that can be dissolved
9.	ICP-MS	inductively coupled plasma with mass spectroscopy	many elements that can be dissolved
10.	SEM	scanning electron microscopy	heavier elements

elements with lower atomic numbers from hydrogen to carbon. More detailed information on each technique is given in Appendix 2B.1.

2.2.7 Elemental and Organic Carbon in Particulate Matter

Ambient particles from combustion sources contain carbon in several chemically and optically distinct forms. Health- and visibility-related studies of these particles require information about the relative contributions to total particle mass by these different forms of carbon. With the exception of carbonate-based carbon, however, a clear classification scheme has not yet been established to distinguish organic carbon, light-absorbing carbon, black carbon, soot and elemental carbon. The absence of clear, physically-based definitions results in confusion in the interpretation of speciation data. For example, depending on the radiation wavelength specified, "light absorbing" carbon can include compounds that volatilize without oxidation. "Black" carbon includes various mixtures containing "elemental" (graphitic) carbon;

1 partially degraded, oxidized graphitic fragments; and partially-oxidized amorphous aromatic
2 carbon. For studying visibility reduction, a measurement of light-absorbing carbon may be more
3 useful than one of elemental carbon. For source apportionment by receptor models, several
4 consistent but distinct fractions of carbon in both source and receptor samples are desired,
5 regardless of their light-absorbing or chemical properties. Differences in ratios of the carbon
6 concentrations in these fractions form part of the source profiles that distinguish the contribution
7 of one source from the contributions of other sources (Watson et al., 1994a,b).

8 Three method-dependent operational classes of carbon are commonly measured in ambient
9 aerosol samples collected on quartz-fiber filters: (1) semi-volatile organic or non-visible light-
10 absorbing carbon, termed "organic carbon (OC)"; (2) elemental carbon, soot, black carbon, or
11 light-absorbing carbon, termed "elemental carbon (EC)"; and (3) carbon present as K_2CO_3 ,
12 Na_2CO_3 , $MgCO_3$, $CaCO_3$, termed "carbonate carbon (CC)." The sum of OC, EC, and CC in PM
13 gives the total carbon (TC).

14 The thermal/optical reflectance (TOR), thermal/optical transmission (TOT), and thermal
15 manganese oxidation (TMO) methods are most commonly used for the analysis of organic and
16 elemental carbon in atmospheric PM. In thermal separation methods, OC is vaporized and the
17 EC remaining on the filter is then oxidized to CO_2 and quantified by nondispersive infrared
18 detection, by electrochemical techniques or by reducing the CO_2 to CH_4 and quantifying CH_4 via
19 flame ionization detection (FID). OC that does not vaporize below 550 C can pyrolyze at higher
20 temperatures to form additional black carbon. Thermal/optical methods must correct for this
21 effect in order to correctly distinguish OC from EC. The various methods give similar results for
22 TC, but not for EC or OC, due to differing assumptions regarding the thermal behavior of
23 ambient aerosol carbon. These methods are discussed in detail in Appendix 2B.2.

24 Carbonate carbon (i.e., K_2CO_3 , Na_2CO_3 , $MgCO_3$, $CaCO_3$) can be determined thermally, or
25 on a separate filter section by measurement of the carbon dioxide (CO_2) evolved upon
26 acidification (Johnson et al., 1980). It is usually on the order of 5% or less of TC for ambient
27 particulate samples collected in urban areas (Appel, 1993).

28 The forms of carbon present in natural materials that may be burnt to generate atmospheric
29 aerosol tend to be poorly defined. Thus, the pyrolysis products of these materials during
30 thermal/optical analysis cannot be predicted. The Geochemical Society convened an
31 international steering committee in 1999 to define a set of representative black carbon and black

1 carbon-containing benchmark materials to be used to support ambient aerosol sample analysis.
2 These standard materials may be used to provide thermal/optical "fingerprints" for deducing
3 primary aerosol sources, and to establish characteristic analytic interferences or artifacts
4 associated with such sources. The materials recommended to date include n-hexane soot,
5 lignocellulosic chars, soils, marine sediments, and the NIST urban dust standard reference
6 material (SRM 1649a). The committee has also recommended a set of standard materials that
7 may potentially interfere with black carbon analyses: shale, natural organic matter, melanoidin
8 (an amino acid-based material) and coals. These recommendations are discussed on the steering
9 committee website: <http://www.du.edu/~dwismith/bcsteer.html>.

11 **2.2.8 Ionic Species**

12 Ion chromatography (IC) is widely used for analyzing ionic species in the water-soluble
13 portion of suspended PM. IC is the method of choice for the measurement of sulfate, nitrate,
14 ammonium, sodium, and potassium ions for the NAMS program. Aerosol strong acidity, H^+ , is
15 determined by titration of a water solution of PM collected following a series of annular
16 denuders to remove acid and basic gases with back-up filters to collect NH_3 and HNO_3 that
17 volatilize from the PM during collection. The 1996 PM AQCD (U.S. Environmental Protection
18 Agency, 1996a) discussed measurement of ions by IC (Section 4.3.3.1) and of strong acidity
19 (Sections 3.3.1.1 and 4.3.3.1); so, no further details will be discussed here.

21 **2.2.9 Continuous Monitoring**

22 The EPA expects that many local environmental agencies will operate continuous PM
23 monitors. All currently available continuous measurements of suspended particle mass share the
24 problem of dealing with semivolatile PM components. So as not to include particle-bound water
25 as part of the mass, the particle-bound water must be removed by heating or dehumidification.
26 However, heating also causes loss of ammonium nitrate and semivolatile organic components.
27 A variety of potential candidates for continuous measurement of particle mass and related
28 properties are listed in Table 2-6. These techniques are discussed in more detail in Appendix
29 2B.3.

TABLE 2-6. METHODS FOR CONTINUOUS MEASUREMENT OF PM MASS, COMPONENTS, ETC.

#	Acronym	Name	Comments
1.	TEOM	Tapered Element Oscillating Microbalance	Measures only nonvolatile components of PM.
2.	TEOM with SES	TEOM with Sample Equilibration System	By using dehumidification instead of heat for drying and a lower temperature for stabilization, includes some of the semivolatile components of PM.
3.	—	Differential TEOM	Research instrument designed to measure both the nonvolatile and semivolatile components of PM.
4.	FDMS	Filter Dynamics Measurement System	Commercial version of the differential TEOM.
5.	RAMS	Real-Time Total Ambient Mass Sampler	Research instrument designed to measure total PM using denuders and an adsorptive filter.
6.	CAMM	Continuous Ambient Mass Monitor	Measures total PM by pressure drop across a frequently changed filter.
7.	—	Beta gauge	Measures PM mass by beta attenuation. Unless dried by heat or dehumidification will also measure particle-bound water.
8.	—	Piezoelectric microbalance	Measures mass by change in resonance frequency when particles are deposited on a crystal.
9.	CCPM	Continuous Coarse Particle Monitor	Virtual impaction is used to concentrate PM _{10-2.5} which is then measured by a TEOM.
10.	—	Semi-continuous EC/OC	Several commercially available instruments automate the thermal technique for EC/OC and provide hourly measurements.
11.	—	Semi-continuous nitrate	Collection of PM followed by flash vaporization and determination of NO _x provides 10 minute measurements of particulate nitrate.
12.	—	Semi-continuous sulfate	Several techniques are available in which particulate sulfate is measured using flame ionization detection.
13.	—	Continuous ion chromatography of water-soluble ions	Particles are grown by mixing with water vapor, collected in water, and injected into an automatic ion chromatography.
14.	—	Mass spectroscopy of individual particles	Single particles are evaporated, ionized and the components analyzed by mass spectroscopy. Several different systems are in use in research studies.
15.	EAD	Electrical Aerosol Detector	This instrument measures charge collected by particles and gives a continuous signal that is proportional to the integral of the particle diameter.
16.	—	Integrating nephelometer	Light scattering by suspended particles, collected over a large solid angle, provides an indicator for particle mass including particle-bound water unless the air sample is dried by heating or dehumidification.

2.2.10 Measurements of Individual Particles

Recently, several researchers have developed instruments for real-time *in situ* analysis of single particles (e.g., Noble and Prather, 1996; Gard et al., 1997; Johnson and Wexler, 1995; Silva and Prather, 1997; Thomson and Murphy, 1994). Although the technique varies from one laboratory to another, the underlying principle is to fragment each particle into ions, using either a high-power laser or a heated surface and, then, a time-of-flight mass spectrometer (TOFMS) to measure the ion fragments in a vacuum. Each particle is analyzed in a suspended state in the air stream (i.e., without collection), avoiding sampling artifacts associated with impactors and filters. The technique is called aerosol time-of-flight mass spectrometry (ATOFMS). By measuring both positive and negative ions from the same particle, information can be obtained about the composition, of individual particles of known aerodynamic diameter. This information is especially useful in determining sources of particles. Noble and Prather (1996) used ATOFMS to provide compositionally resolved particle-size distributions. Their instrument is capable of analyzing size and chemical composition of 50 to 100 particles/min at typical ambient concentrations and up to 600/min at high particle concentrations. Four systems for measurement of single particles using mass spectroscopy are reviewed by Middlebrook (2002). An example of the type of information that can be determined is shown in Figure 2-25.

Because particles are analyzed individually, biases in particle sampling (the efficiency of particle transmission into the sensor chamber as a function of size; particle size measurement, and detection of particles prior to fragmentation) represent a major challenge for these instruments. Moreover, the mass spectrometer has a relatively large variability in ion yields (i.e., identical samples would yield relatively large differences in mass spectrometer signals [Thomson and Murphy, 1994]); therefore, quantitation is inherently difficult (Murphy and Thomson, 1997). Quantitation will be even more challenging for complex organic mixtures because of the following two reasons: (1) a large number of fragments are generated from each molecule, and (2) ion peaks for organics can be influenced or obscured by inorganic ions (Middlebrook et al., 1998). Nonetheless, scientists have been successful in using these techniques to identify the presence of organics in atmospheric particles and laboratory-generated particles (i.e., as contaminants in laboratory-generated sulfuric acid droplets) as well as the identification of specific compound classes such as PAHs in combustion emissions (Castaldi and Senkan, 1998; Hinz et al., 1994; Middlebrook et al., 1998; Murphy and Thomson, 1997;

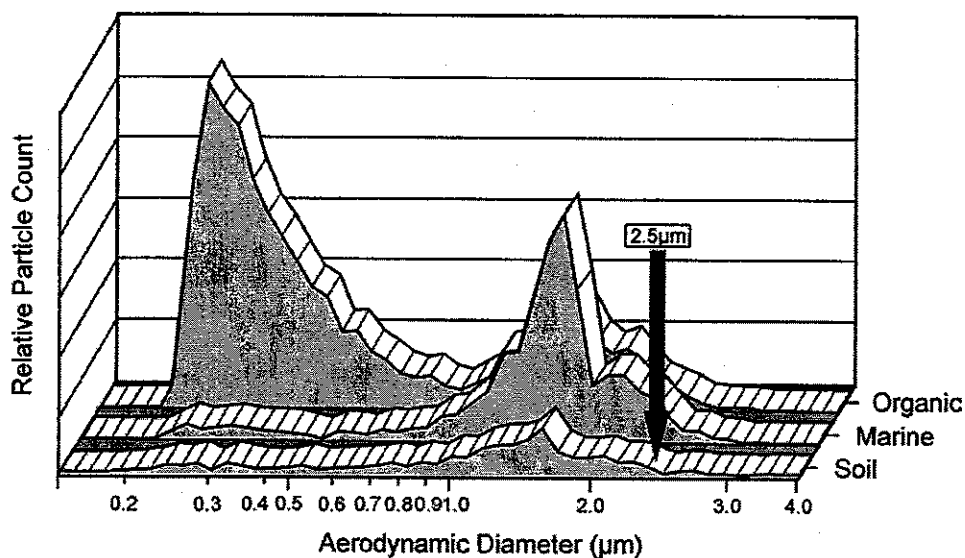


Figure 2-25. Size distribution of particles divided by chemical classification into organic, marine, and crustal.

Source: Noble and Prather (1998).

Neubauer et al., 1998; Noble and Prather, 1998; Reilly et al., 1998; Silva and Prather, 1997). A new multivariate technique for calibration of ATOFMS using microorifice impactors shows promise for simplifying the calibration process (Ferguson et al., 2001). This calibration technique has been applied to gasoline and diesel particles to demonstrate the feasibility of using this technique for the source apportionment of gasoline and diesel particles in an atmospheric mixture (Song et al., 2001).

Until recently, ATOFMS systems have only been able to characterize particles that are larger than approximately 0.2 to 0.3 μm in diameter. Wexler and colleagues (Carson et al., 1997; Ge et al., 1998) have developed an ATOFMS instrument that is able to size, count, and provide chemical composition on individual particles ranging in size from 10 nm to 2 μm .

2.2.11 Low Flow Filter Samples for Multiday Collection of Particulate Matter

For some purposes, such as demonstrating attainment of an annual standard or as an exposure indicator for epidemiologic studies of chronic health effects, 24-h measurements are not essential. Annual or seasonal averages may be adequate. Multiday sampling techniques can result in lower costs for weighing, chemical analysis, and travel time to change filters. The multiday sampler serves a second purpose. Most commercially available samplers are optimized for collecting 24-h samples of the PM concentrations found in the U.S., Europe, or Japan. Many cities in other parts of the world have significantly higher PM concentrations. Under these conditions, the 16.7 L/min flow through 37 or 47 mm diameter filters may overload the filter and prevent the sampler from maintaining the prescribed flow rate for 24 h. A low flow sampler with a 0.4 L/min flow rate and a 47 mm diameter filter has been designed by Aerosol Dynamics, Inc. With this sampler, the sample collection time can be chosen to suit the ambient concentration level. This sampler, with a one-week collection period, has been used to characterize PM_{2.5} in Beijing, PRC (He et al., 2001). With a two-week collection period, it is being used in a chronic epidemiologic study in southern California, USA (Gauderman, et al., 2000).

The sampler, as described by He et al. (2001), has three PM_{2.5} channels. One channel collects PM on a Teflon filter for gravimetric mass measurement and elemental analysis by XRF. A second channel collects PM on a quartz filter for organic and elemental carbon analysis. A denuder to remove organic gases and a backup filter to collect semivolatile organic compounds may be added. The third channel uses a carbonate denuder to remove acid gases (HNO₃ and SO₂), a Teflon filter to collect PM for analysis of ions by ion chromatography, and a nylon filter to collect volatilized nitrate. The Teflon filter can also be weighed prior to extraction. Thus, the multiday sampler can provide the information needed for source apportionment by Chemical Element Balance techniques (Watson et al., 1990a,b; U.S. Environmental Protection Agency, 2002b).

For monitoring sites with high day-to-day variability in PM concentrations, a sample integrated over a week may provide a more accurate measurement of the annual average than can be obtained by 1-in-3 or 1-in-6 day sampling schedules. Daily PM data from Spokane, WA were resampled to simulate common sampling schedules and the error due to less-than-everyday sampling was computed (Rumburg et al., 2001). The error in the annual mean concentration for

PM_{2.5}, expressed as a percentage difference from the everyday sampling mean, was 1.7, 3.4, and 7.7% for 1-in-2 day, 1-in-3 day, and 1-in-6 day sampling, respectively.

2.3 SUMMARY AND KEY POINTS

2.3.1 Atmospheric Physics and Chemistry of Particles

Atmospheric particles originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. The composition and behavior of aerosols are linked with those of the surrounding gas. Aerosol may be defined as a suspension of solid or liquid particles in air and includes both the particles and all vapor or gas phase components of air. However, the term aerosol often is used to refer to the suspended particles only.

A complete description of the atmospheric aerosol would include an accounting of the chemical composition, morphology, and size of each particle, and the relative abundance of each particle type as a function of particle size. Recent developments in single particle analysis techniques are bringing such a description closer to reality.

The diameter of a spherical particle may be determined geometrically, from optical or electron microscopy, by light scattering and Mie theory, or by a particle's behavior (e.g., electrical mobility or its aerodynamic behavior). However, the various types of diameters may be different, and atmospheric particles often are not spherical. Therefore, particle diameters are described by an "equivalent" diameter. Aerodynamic diameter, D_a (the diameter of a unit density sphere that would have the same terminal settling velocity as the real particle), and the Stokes diameter, D_p (the diameter of a sphere of the same density as the particle that would have the same aerodynamic resistance or drag), are the most widely used equivalent diameters.

Atmospheric size distributions show that most atmospheric particles are quite small, below 0.1 μm ; whereas most of the particle volume (and therefore most of the mass) is found in particles greater than 0.1 μm . An important feature of the mass or volume size distributions of atmospheric particles is their multimodal nature. Volume distributions, measured in ambient air in the United States, are almost always found to have a minimum between 1.0 and 3.0 μm . That portion of the size distribution that contains particles that are mostly larger than the minimum is called "coarse" particles or the "coarse" mode. That portion of the size distribution that contains

1 particles that are mostly smaller than the minimum is called "fine" particles and includes several
2 modes. "Accumulation-mode" refers to that portion of fine particles with diameters above about
3 0.1 μm . That portion of fine particles with diameters below 0.1 μm are usually called "ultrafine"
4 by toxicologists and epidemiologists and "nanoparticles" by aerosol physicists and material
5 scientists. In the number distribution of ultrafine particles, particles in the size range below 0.01
6 are called the nucleation mode and particles between 0.01 and 0.1 are called the Aitken mode.
7 The Aitken mode can be observed as a separate mode in mass or volume distributions only in
8 clean or remote areas or near sources of new particle formation by nucleation.

9 The aerosol community uses three different approaches or conventions in the classification
10 of particles by size: (1) modes, based on the observed size distributions and formation
11 mechanisms; (2) cut point, usually based on the 50% cut point of the specific sampling device,
12 including legally specified, regulatory sizes for air quality standards; and (3) dosimetry or
13 occupational sizes, based on the entrance into various compartments of the respiratory system.
14 Over the years, the terms fine and coarse as applied to particle sizes have lost the original precise
15 meaning of fine and coarse. In any given article, therefore, the meaning of fine and coarse,
16 unless defined, must be inferred from the author's usage. In particular, $\text{PM}_{2.5}$ and fine particles
17 are not equivalent. $\text{PM}_{2.5}$ refers to the aggregate sample of PM that is collected following a size-
18 selective inlet with a specified penetration as a function of size and a 50% cutpoint of 2.5 μm D_p .
19 It may also be used to refer to number (or other measure of particles suspended in the
20 atmosphere that would be collected by such a sampler). PM_{10} is defined similarly. $\text{PM}_{10-2.5}$
21 refers to the sample that would be collected if the $\text{PM}_{2.5}$ component could be removed from a
22 PM_{10} sample.

23 Several processes influence the formation and growth of particles. New particles may be
24 formed by nucleation from gas phase material. Particles may grow by condensation as gas phase
25 material condenses onto existing particles. Particles may also grow by coagulation as two
26 particles combine to form one. Gas phase material condenses preferentially on smaller particles,
27 and the rate constant for coagulation of two particles decreases as the particle size increases.
28 Therefore, nuclei mode particles grow into the accumulation mode, but growth of accumulation
29 mode particles into the coarse mode is rare.

30 The major constituents of atmospheric PM are sulfate, nitrate, ammonium, and hydrogen
31 ions; particle-bound water; elemental carbon; a great variety of organic compounds; and crustal

1 material. Atmospheric PM contains a large number of elements in various compounds and
2 concentrations and hundreds of specific organic compounds. Particulate material can be primary
3 or secondary. PM is called primary if it is in the same chemical form in which it was emitted
4 into the atmosphere. PM is called secondary if it is formed by chemical reactions in the
5 atmosphere. Primary coarse particles are usually formed by mechanical processes; whereas
6 primary fine particles are emitted from sources either directly as particles or as vapors that
7 rapidly condense to form particles.

8 Most of the sulfate and nitrate and a portion of the organic compounds in atmospheric
9 particles are secondary. Secondary aerosol formation depends on numerous factors including the
10 concentrations of precursors; the concentrations of other gaseous reactive species such as ozone,
11 hydroxyl radical, peroxy radicals, and hydrogen peroxide; atmospheric conditions, including
12 solar radiation and relative humidity; and the interactions of precursors and preexisting particles
13 within cloud or fog droplets or on or in the liquid film on solid particles. As a result, it is
14 considerably more difficult to relate ambient concentrations of secondary species to sources of
15 precursor emissions than it is to identify the sources of primary particles.

16 The lifetimes of particles vary with particle size. Coarse particles can settle rapidly from
17 the atmosphere within minutes or hours and normally travel only short distances. However,
18 when mixed high into the atmosphere, as in dust storms, the smaller-sized, coarse-mode particles
19 may have longer lives and travel greater distances. Accumulation-mode particles are kept
20 suspended by normal air motions and have a lower deposition velocity than coarse-mode
21 particles. They can be transported thousands of kilometers and remain in the atmosphere for a
22 number of days. Accumulation-mode particles are removed from the atmosphere primarily by
23 cloud processes. Dry deposition rates are expressed in terms of a deposition velocity that varies
24 with the particle size, reaching a minimum between 0.1 and 1.0 μm aerodynamic diameter.

25 PM is a factor in acid deposition. Particles serve as cloud condensation nuclei and
26 contribute directly to the acidification of rain. In addition, the gas-phase species that lead to dry
27 deposition of acidity are also precursors of particles. Therefore, reductions in SO_2 and NO_x
28 emissions will decrease both acid deposition and PM concentrations. Sulfuric acid, ammonium
29 nitrate, and organic particles also are deposited on surfaces by dry deposition and can contribute
30 to ecological effects.

2.3.2 Measurement of Atmospheric Particles

The decision by the EPA to revise the PM standards by adding daily and yearly standards for $PM_{2.5}$ has led to a renewed interest in the measurement of atmospheric particles and to a better understanding of the problems in developing precise and accurate measurements of particles. Unfortunately, it is very difficult to measure and characterize particles suspended in the atmosphere.

PM monitoring is used to develop information to guide implementation of standards (i.e., to identify sources of particles; to determine whether or not a standard has been attained; and to determine health, ecological, and radiative effects). Federal Reference Methods (FRM) specify techniques for measuring PM_{10} and $PM_{2.5}$. Particles are collected on filters and mass concentrations are determined gravimetrically. The PM_{10} FRM sampler consists of a PM_{10} inlet/impactor and a 47-mm Teflon filter with a particle collection efficiency greater than 99.7%. The $PM_{2.5}$ FRM is similar except that it includes a $PM_{2.5}$ impactor with an oil-covered impaction substrate to remove particles larger than $2.5\ \mu m$. Both techniques provide relatively precise ($\pm 10\%$) methods for determining the mass of material remaining on a Teflon filter after equilibration. Despite considerable progress in measuring the atmospheric PM mass concentration, numerous uncertainties continue to exist as to the relationship between the mass and composition of material remaining on the filter as measured by the FRMs and the mass and composition of material that exists in the atmosphere as suspended PM. There is no reference standard for particles suspended in the atmosphere, nor is there an accepted way to remove particle-bound water without losing some of the semivolatile components of PM such as ammonium nitrate and semivolatile organic compounds. It also is difficult to cleanly separate fine and coarse PM. As a result, EPA defines accuracy for PM measurements in terms of agreement of a candidate sampler with a reference sampler. Therefore, intercomparisons of samplers become very important in determining how well various samplers agree and how various design choices influence what is actually measured.

Current filtration-based mass measurements lead to significant evaporative losses of a variety of semivolatile components (i.e., species that exist in the atmosphere in dynamic equilibrium between the condensed phase and gas phase) during and possibly after collection. Important examples include ammonium nitrate, semivolatile organic compounds, and particle-bound water. Loss of these components may significantly affect the quality of the measurement

1 and can lead to both positive and negative sampling artifacts. Negative artifacts resulting from
2 loss of ammonium nitrate and semivolatile organic compounds may occur during sampling
3 because of changes in temperature, relative humidity, or composition of the aerosol or because
4 of the pressure drop across the filter. Negative artifacts also may occur during handling and
5 storage because of evaporation. Positive artifacts occur when gas-phase compounds (H_2O ,
6 HNO_3 , SO_2 , and organic compounds) absorb onto or react with filter media or collected PM or
7 when some particle-bound water is not removed.

8 Sampling systems for semivolatile PM components make use of denuders to remove the
9 gas-phase fraction and absorptive filters to remove the condensed phase and retain any material
10 that subsequently evaporates from the collected PM. The loss of particulate nitrate may be
11 determined by comparing nitrate collected on a Teflon filter to that collected on a nylon filter
12 (which absorbs nitric acid which evaporates from ammonium nitrate particles) preceded by a
13 denuder to remove gas-phase nitric acid. In two studies in southern California, the $\text{PM}_{2.5}$ mass
14 lost because of volatilization of ammonium nitrate was found to represent 10 to 20% of the total
15 $\text{PM}_{2.5}$ mass and almost a third of the nitrate. Denuder/absorptive filter sampling systems also
16 have been developed for measuring particulate phase organic compounds. This technique is an
17 improvement over the filter/adsorbent collection method. However, the denuder systems
18 currently discussed in the literature are not straightforward in their use, and the user must have a
19 thorough understanding of the technology. The FRM for $\text{PM}_{2.5}$ will likely suffer loss of
20 particulate nitrates and semivolatile organic compounds, similar to the losses experienced with
21 other single filter collection systems.

22 It is generally desirable to collect and measure ammonium nitrate and semivolatile organic
23 compounds as part of particulate matter mass. However, it is usually desirable to remove the
24 particle-bound water before determining the mass. In some situations, it may be important to
25 know how much of the suspended particle's mass or volume results from particle-bound water.
26 Calculations and measurements indicate that aerosol water content is strongly dependent on
27 relative humidity and composition. Particle-bound water can represent a significant mass
28 fraction of the PM concentration at relative humidities above 60%. A substantial fraction of
29 accumulation-mode PM is hygroscopic or deliquescent. The more hygroscopic particles tend to
30 contain more sulfates, nitrates, and secondary organic compounds, while the less hygroscopic
31 particles tend to contain more elemental carbon, primary organic compounds, and crustal

1 components. Fresh, submicron-size soot particles may tend to shrink with increasing relative
2 humidity because of a structural change. The effects of relative humidity on the sorption of
3 semivolatile organic compounds on particles are not well understood. The amount of water
4 sorbed to an atmospheric aerosol may be affected by the presence of an organic film on the
5 particle, which may impede the transport of water across the surface.

6 Fine and coarse particles differ not only in formation mechanisms and size, but also in
7 sources; composition; and chemical, physical, and biological properties. Fine and coarse
8 particles overlap in the intermodal size range (1-2.5 $\mu\text{m D}_p$). As relative humidity increases, fine
9 particles grow into this size range; as relative humidity decreases, more coarse particles may be
10 suspended in this size range. It is desirable to measure fine PM and coarse PM separately in
11 order to properly allocate health effects to either fine PM or coarse PM and to correctly
12 determine sources by factor analysis or chemical mass balance. The selection of a cut point of
13 2.5 μm as a basis for EPA's 1997 NAAQS for fine particles (Federal Register, 1997) and its
14 continued use in many health effects studies reflects the importance placed on more complete
15 inclusion of accumulation-mode particles, while recognizing that intrusion of coarse-mode
16 particles can occur under some conditions with this cut point.

17 In addition to FRM sampling of equilibrated mass to determine compliance with PM
18 standards, EPA requires states to conduct speciation sampling primarily to determine source
19 categories and trends. The current speciation samplers collect $\text{PM}_{2.5}$ on three filters:
20 (1) a Teflon filter for gravimetric determination of mass and for analysis of heavy elements by
21 X-ray fluorescence; (2) a Nylon filter preceded by a nitric acid denuder for artifact-free
22 determination of nitrate and measurement of other ionic species by ion chromatography; and
23 (3) a quartz filter for measurement of elemental carbon (EC) and organic carbon (OC). In
24 addition, IMPROVE (Interagency Monitoring of Protected Visual Environments) samplers
25 provide information on regional PM background and transport. IMPROVE samplers, in addition
26 to the three types of filters collected by the speciation samplers, also collect a PM_{10} sample. The
27 IMPROVE and speciation networks use slightly different methods for determination of EC and
28 OC. The two methods agree on total carbon but differ in the split of total carbon into EC and
29 OC. The two methods also differ in their correction for positive artifacts due to absorption of
30 volatile organic compounds on the quartz filters. Neither EC/OC method provides for any

1 correction for negative artifacts due to evaporation of semivolatile organic compounds from the
2 collected particles.

3 The EPA expects that monitoring agencies will operate continuous PM monitors; and EPA
4 is in the process of providing guidance regarding appropriate continuous monitoring techniques.
5 All currently available techniques for continuous measurements of suspended particle mass, e.g.,
6 the integrating nephelometer, the beta-absorption monitor, and the Tapered Element Oscillating
7 Microbalance (TEOM), share the problem of dealing with semivolatile PM components: that is,
8 in order not to include particle-bound water as part of the mass, the particle-bound water must be
9 removed by heating or dehumidification; however, heating also causes ammonium nitrate and
10 semivolatile organic compounds to evaporate. The TEOM monitor operates at a constant, but
11 higher than ambient, temperature to remove particle-bound water; whereas, the FRM is required
12 to operate at no more than 5 °C above the ambient temperature. Subsequently, much of the
13 particle-bound water is removed during equilibration at 40% relative humidity. This difference
14 in techniques for removal of particle-bound water causes differences in the measured mass
15 concentration between the TEOM and FRMs.

16 Several new techniques for continuous PM mass measurements are currently being field
17 tested. The Real-Time Total Ambient Mass Sampler (RAMS) measures the total mass of
18 collected particles including semivolatile species with a TEOM monitor using a "sandwich
19 filter." The sandwich contains a Teflon-coated particle-collection filter followed by a charcoal-
20 impregnated filter to collect any semivolatile species lost from the particles during sampling.
21 The RAMS uses a Nafion dryer to remove particle-bound water from the suspended particles and
22 a particle concentrator to reduce the quantity of gas phase organic compounds that must be
23 removed by the denuder. The Continuous Ambient Mass Monitor (CAMM) estimates ambient
24 particulate matter mass by measurement of the increase in the pressure drop across a membrane
25 filter caused by particle loading. It also uses a Nafion dryer to remove particle-bound water.
26 A new differential TEOM offers the possibility of measuring both nonvolatile and semivolatile
27 PM mass. In addition to continuous mass measurement, a number of techniques for continuous
28 measurement of sulfate, nitrate, or elements are being tested.
29
30
31

2.3.3 Key Points

Fine and Coarse Particles

Particle size distributions show that atmospheric particles exist in two classes, fine particles and coarse particles. Fine and coarse particles are defined primarily in terms of their formation mechanisms and size; an they also differ in sources, chemical composition, and removal processes (see Table 2-1). Subsequent chapters will show that fine and coarse particles also differ in aspects of concentration, exposure, dosimetry, toxicology, and epidemiology.

These differences support the setting of separate standards for fine and coarse particles. Fine and coarse particles overlap in the size range between 1 and 3 μm aerodynamic diameter where particulate matter (PM) concentrations are at a minimum. Coarse particles are generally larger than this minimum and are generally formed by mechanical processes. Coarse particles and coarse-mode particles are equivalent terms. Fine particles are generally smaller than the minimum and are generally formed by coagulation and condensation of gases. Fine particles are subdivided into accumulation, Aitkin, and nucleation modes. In earlier texts, nuclei mode referred to the size range now split into the Aitkin and nucleation modes (see Figures 2-4 and 2-5).

Measurement of Mass and Composition

Nonvolatile PM. Analytical techniques exist for measurement of the mass and chemical composition of PM retained on a filter (nonvolatile mass) in terms of elements (except carbon) and certain key ions (sulfate, nitrate, hydrogen, and ammonium). Acceptable measurements can be made of the total carbon retained on a filter. However, the split into organic carbon and elemental carbon depends on the operational details of the analytical methods and varies somewhat among methods. Determination of the various organic compounds in the organic carbon fraction remains a challenge.

Semivolatile PM. Important components of atmospheric PM (particle-bound water, ammonium nitrate, and many organic compounds) are termed semivolatile because significant amounts of both the gaseous and condensed phases may exist in the atmosphere in equilibrium. Particle-bound water is not considered a pollutant. Most of the particle-bound water is removed by heating the particles or by equilibration of the collected particles at a low relative humidity

(40%) for 24 hours. However, these processes also cause the loss of other semivolatile components. Semivolatile components also evaporate from the filter during sampling due to the pressure drop across the filter or due to a reduction in the atmospheric concentration during the sampling time. Filter collection and equilibration techniques for PM, such as prescribed by the Federal Reference Methods, lose a fraction of the semivolatile PM. Continuous methods must dry the PM to remove particle-bound water. If heating is used to dry the particles, more of the semivolatile components may be removed than are lost in filter sampling. Collection and retention of ammonium nitrate and semivolatile organic compounds represents a major challenge in the effort to move to continuous measurement of PM mass. The use of diffusion dryers, which dehumidify the air stream without heating, represents a promising approach. Uncertainty in the efficiency of retention of ammonium nitrate and organic compounds on filters also impacts source category attribution and epidemiologic studies.

Separation of Fine and Coarse PM

Techniques are available to separate fine particles from coarse particles and collect the fine particles on a filter. No such technique exists for coarse particles. As yet, no consensus exists on the best technique for collecting a coarse particle sample for determination of mass and composition. Candidates include multistage impaction, virtual impaction, and difference (subtracting $PM_{2.5}$ mass or composition from PM_{10} mass or composition). Advances in the theory and practice of virtual impaction suggest that it would be possible to design virtual impactors with much less than the 10% of fine PM collected in the coarse PM sample as is now the case for the dichotomous samplers used in air quality studies and with penetration curves as sharp as those used in the current Federal Reference Method for $PM_{2.5}$.

REFERENCES

- 1 Aiginger, H. (1991) Historical development and principles of total reflection x-ray fluorescence analysis (TXRF).
2 Spectrochim. Acta Part B 46: 1313-1321.
- 3 Aiginger, H.; Strel, C. (1997) Total reflection x-ray fluorescence spectrometry (TXRF) for trace element analysis.
4 Spectrosc. Eur. 9: 16-21.
- 5 Allen, G.; Sioutas, C.; Koutrakis, P.; Reiss, R.; Lurmann, F. W.; Roberts, P. T. (1997) Evaluation of the TEOM®
6 method for measurement of ambient particulate mass in urban areas. J. Air Waste Manage. Assoc.
7 47: 682-689.
- 8 Allen, G. A.; Oh, J. A.; Koutrakis, P.; Sioutas, C. (1999a) Techniques for high-quality ambient coarse particulate
9 mass measurements. J. Air Waste Manage. Assoc. 49(special issue): PM133-PM141.
- 10 Allen, J. O.; Paschkewitz, J. S.; Plummer, E. F.; Lafleur, A. L.; Sarofim, A. F.; Smith, K. A. (1999b) Absorption of
11 semi-volatile compounds in oiled impaction substrates: measurement of pyrene absorption. Aerosol Sci.
12 Technol. 30: 16-29.
- 13 Allen, G. A.; Lawrence, J.; Koutrakis, P. (1999c) Field validation of a semi-continuous method for aerosol black
14 carbon (aethalometer) and temporal patterns of summertime hourly black carbon measurements in
15 southwestern PA. Atmos. Environ. 33: 817-823.
- 16 Allen, R.; Box, M.; Larson, T. V.; Liu, L. J. (2001) A cost-effective weighing chamber for particulate matter filters.
17 J. Air Waste Manage. Assoc. 51: 1650-1653.
- 18 American Conference of Governmental Industrial Hygienists. (1994) 1994-1995 threshold limit values for chemical
19 substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of
20 Governmental Industrial Hygienists.
- 21 Andrews, E.; Larson, S. M. (1993) Effect of surfactant layers on the size changes of aerosol particles as a function of
22 relative humidity. Environ. Sci. Technol. 27: 857-865.
- 23 Andrews, E.; Saxena, P.; Musarra, S.; Hildemann, L. M.; Koutrakis, P.; McMurry, P. H.; Olmez, I.; White, W. H.
24 (2000) Concentration and composition of atmospheric aerosols from the 1995 SEAVS experiment and a
25 review of the closure between chemical and gravimetric measurements. J. Air Waste Manage. Assoc.
26 50: 648-664.
- 27 Appel, B. R. (1993) Atmospheric sample analysis and sampling artifacts. In: Willeke, K.; Baron, P. A., eds. Aerosol
28 measurement: principles, techniques, and applications. New York, NY: Van Nostrand Reinhold; pp. 233-259.
- 29 Appel, B. R.; Tokiwa, Y.; Haik, M. (1981) Sampling of nitrates in ambient air. Atmos. Environ. 15: 283-289.
- 30 Appel, B. R.; Tokiwa, Y.; Haik, M.; Kothny, E. L. (1984) Artifact particulate sulfate and nitrate formation on filter
31 media. Atmos. Environ. 18: 409-416.
- 32 Arnott, W. P.; Moosmüller, H.; Rogers, C. F.; Jin, T.; Bruch, R. (1999) Photoacoustic spectrometer for measuring
33 light absorption by aerosol; instrument description. Atmos. Environ. 33: 2845-2852.
- 34 Arnott, W. P.; Moosmüller, H.; Walker, J. W. (2000) Nitrogen dioxide and kerosene-flame soot calibration of
35 photoacoustic instruments for measurement of light absorption by aerosols. Rev. Sci. Instruments
36 71: 4545-4552.
- 37 Ayers, G. P.; Keywood, M. D.; Gras, J. L. (1999) TEOM vs. manual gravimetric methods for determination of PM_{2.5}
38 aerosol mass concentrations. Atmos. Environ. 33: 3717-3721.
- 39 Babich, P.; Davey, M.; Allen, G.; Koutrakis, P. (2000) Method comparisons for particulate nitrate, elemental carbon,
40 and PM_{2.5} mass in seven U.S. cities. J. Air Waste Manage. Assoc. 50: 1095-1105.
- 41 Bacon, J. R.; Chenery, S. R. N.; Ellis, A. T.; Fisher, A.; McMahon, A. W.; Potts, P. J.; Williams, J. G. (1995)
42 Atomic spectrometry update—atomic mass spectrometry and x-ray fluorescence spectrometry. J. Anal. At.
43 Spectrom. 10: 253R-310R.
- 44 Baldwin, D. P.; Zamzow, D. S.; D'Silva, A. P. (1994) Aerosol mass measurement and solution standard additions for
45 quantitation in laser ablation-inductively coupled plasma atomic emission spectrometry. Anal. Chem.
46 66: 1911-1917.
- 47 Ballach, J.; Hitzengerger, R.; Schultz, E.; Jaeschke, W. (2001) Development of an improved optical transmission
48 technique for black carbon (BC) analysis. Atmos. Environ. 35: 2089-2100.
- 49 Baron, P. A.; Willeke, K., eds. (2002) Aerosol measurement: principles, techniques, and applications. 2nd ed.
50 New York, NY: John Wiley & Sons.
- 51 Benner, R. L.; Stedman, D. H. (1989) Universal sulfur detection by chemiluminescence. Anal. Chem.
52 61: 1268-1271.
- 53 Benner, R. L.; Stedman, D. H. (1990) Field evaluation of the sulfur chemiluminescence detector. Environ. Sci.
54 Technol. 24: 1592-1596.

- 1 Bergin, M. H.; Ogren, J. A.; Schwartz, S. E.; McInnes, L. M. (1997) Evaporation of ammonium nitrate aerosol in a
2 heated nephelometer: implications for field measurements. *Environ. Sci. Technol.* 31: 2878-2883.
- 3 Bertoni, G.; Febo, A.; Perrino, C.; Possanzini, M. (1984) Annular active diffuse sampler: a new device for the
4 collection of organic vapours. *Ann. Chim. (Rome)* 74: 97-104.
- 5 Billiet, J.; Dams, R.; Hoste, J. (1980) Multielement thin film standards for XRF analysis. *X-Ray Spectrom.*
6 9: 206-211.
- 7 Binkowski, F. S.; Ching, J. K. S. (1995) Modeling fine particulate mass and visibility using the EPA regional
8 particulate model. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Research
9 and Development, National Exposure Research Laboratory; report no. EPA/600/A-95/143. Available from:
10 NTIS, Springfield, VA; PB96-139100.
- 11 Binkowski, F. S.; Shankar, U. (1995) The regional particulate matter model. I. Model description and preliminary
12 results. *J. Geophys. Res. [Atmos.]* 100: 26,191-26,209.
- 13 Birch, M. E. (1998) Analysis of carbonaceous aerosols: interlaboratory comparison. *Analyst (Cambridge, UK)*
14 123: 851-857.
- 15 Birch, M. E.; Cary, R. A. (1996) Elemental carbon-based method for occupational monitoring of particulate diesel
16 exhaust: methodology and exposure issues. *Analyst* 121: 1183-1190.
- 17 Birmili, W.; Wiedensohler, A. (1998) The influence of meteorological parameters on ultrafine particle production at
18 a continental site. *J. Aerosol Sci.* 29(suppl. 1): S1015-S1016.
- 19 Bowers, W. D.; Chuan, R. L. (1989) Surface acoustic-wave piezoelectric crystal aerosol mass monitor. *Rev. Sci.*
20 *Instrum.* 60: 1297-1302.
- 21 Brauer, M.; Koutrakis, P.; Keeler, G. J.; Spengler, J. D. (1991) Indoor and outdoor concentrations of inorganic acidic
22 aerosols and gases. *J. Air Waste Manage. Assoc.* 41: 171-181.
- 23 Breum, N. O. (2000) The dust holding capacity of porous plastic foam used in particle size-selective sampling.
24 *J. Aerosol Sci.* 31: 379-385.
- 25 Brook, J. R.; Dann, T. F. (1999) Contribution of nitrate and carbonaceous species to PM_{2.5} observed in Canadian
26 cities. *J. Air Waste Manage. Assoc.* 49: 193-199.
- 27 Brorström, E.; Grennfelt, P.; Lindskog, A. (1983) The effect of nitrogen dioxide and ozone on the decomposition of
28 particle-associated polycyclic aromatic hydrocarbons during sampling from the atmosphere. *Atmos. Environ.*
29 17: 601-605.
- 30 Bukowiecki, N.; Kittelson, D. B.; Watts, W. F.; Burtcher, H.; Weingartner, E.; Baltensperger, U. (2002) Real-time
31 characterization of ultrafine and accumulation mode particles in ambient combustion aerosols. *J. Aerosol Sci.*
32 33: 1139-1154.
- 33 Bunz, H.; Koyro, M.; Möhler, O.; Saathoff, H. (1996) Temperature dependence of the redistribution mechanisms for
34 volatile components of atmospheric aerosol particles. *J. Aerosol Sci.* 27(suppl. 1): S653-S654.
- 35 Cachier, H.; Bremond, M.-P.; Buat-Ménard, P. (1989) Determination of atmospheric soot carbon with a simple
36 thermal method. *Tellus* 41B: 379-390.
- 37 Cadle, S. H.; Groblicki, P. J. (1982) An evaluation of methods for the determination of organic and elemental carbon
38 in particulate samples. In: Wolff, G. T.; Klimisch, R. L., eds. *Particulate carbon: atmospheric life cycle*. New
39 York, NY: Plenum Press; pp. 89-109.
- 40 Cadle, S. H.; Groblicki, P. J.; Mulawa, P. A. (1983) Problems in the sampling and analysis of carbon particles.
41 *Atmos. Environ.* 17: 593-600.
- 42 Cadle, S. H.; Mulawa, P. A. (1990) Atmospheric carbonaceous species measurement methods comparison study:
43 General Motors results. *Aerosol Sci. Technol.* 12: 128-131.
- 44 Cahill, T. A. (1981) Innovative aerosol sampling devices based upon PIXE capabilities. In: Johansson, S. A. E., ed.
45 *Particle induced x-ray emission and its analytical applications: proceedings of the 2nd international*
46 *conference on PIXE and its analytical applications; June, 1980; Lund, Sweden. Amsterdam, The Netherlands:*
47 *North-Holland Publishing Co. Nucl. Instr. Meth. Phys. Res.* 181: 473-480.
- 48 Cahill, T. A. (1985) Proton-induced X-ray emission (PIXE). In: Res, J. P., ed. *Metals Handbook: Materials*
49 *Characterization*. Cleveland, OH: American Society for Metals.
- 50 Cahill, T. A. (1990) Particle-induced x-ray emission. In: Mills, K., ed. *Metals Handbook; v. 10, p. 102. 9th ed.*
51 *Cleveland, OH: American Society for Metals.*
- 52 Cahill, T. A.; Eldred, R. A.; Motallebi, N.; Malm, W. C. (1989) Indirect measurement of hydrocarbon aerosols
53 across the United States by nonsulfate hydrogen-remaining gravimetric mass correlations. *Aerosol Sci.*
54 *Technol.* 10: 421-429.
- 55 Cahill, T. A.; Wilkinson, K.; Schnell, R. (1992) Composition analyses of size-resolved aerosol samples taken from
56 aircraft downwind of Kuwait, spring 1991. *J. Geophys. Res. [Atmos.]* 97: 14,513-14,520.

- 1 Cahill, T. A.; Wakabayashi, P.; James, T. A. (1996) Chemical states of sulfate at Shenandoah National Park during
2 summer, 1991. *Nucl. Instrum. Methods Phys. Res. B* 109/110: 542-547.
- 3 Camp, D. C.; Stevens, R. K.; Cobourn, W. G.; Husar, R. B.; Collins, J. F.; Huntzicker, J. J.; Husar, J. D.; Jaklevic,
4 J. M.; McKenzie, R. L.; Tanner, R. L.; Tesch, J. W. (1982) Intercomparison of concentration results from fine
5 particle sulfur monitors. *Atmos. Environ.* 16: 911-916.
- 6 Campbell, A. J.; Humayun, M. (1999) Trace element microanalysis in iron meteorites by laser ablation ICPMS.
7 *Anal. Chem.* 71: 939-946.
- 8 Carson, P. G.; Johnston, M. V.; Wexler, A. S. (1997) Laser desorption/ionization of ultra fine aerosol particles.
9 *Rapid Commun. Mass Spectrom.* 11: 993-996.
- 10 Castaldi, M. J.; Senkan, S. M. (1998) Real-time, ultrasensitive monitoring of air toxics by laser photoionization
11 time-of-flight mass spectroscopy. *J. Air Waste Manage. Assoc.* 48: 77-81.
- 12 Chandramouli, B.; Kamens, R. (2001) The photochemical formation and gas-particle partitioning of oxidation
13 products of decamethyl cyclopentasiloxane and decamethyl tetrasiloxane in the atmosphere. *Atmos. Environ.*
14 35: 87-95.
- 15 Chandramouli, B.; Jang, M.; Kamens, R. M. (2003) Gas-particle partitioning of semi-volatile organics on organic
16 aerosols using a predictive activity coefficient model: analysis of the effects of parameter choices on model
17 performance. *Atmos. Environ.* 37: 853-864.
- 18 Chang, M.; Kim, S.; Sioutas, C. (1999) Experimental studies on particle impaction and bounce: effects of substrate
19 design and material. *Atmos. Environ.* 33: 2313-2322.
- 20 Chang, M. C.; Sioutas, C.; Kim, S.; Gong, H., Jr.; Linn, W. S. (2000) Reduction of nitrate losses from filter and
21 impactor samplers by means of concentration enrichment. *Atmos. Environ.* 34: 85-98.
- 22 Chang, M.-C.; Geller, M. D.; Sioutas, C.; Fokkens, P. H. B.; Cassee, F. R. (2002) Development and evaluation of a
23 compact, highly efficient coarse particle concentrator for toxicological studies. *Aerosol Sci. Technol.*
24 36: 492-501.
- 25 Chein, H.; Lundgren, D. A. (1993) A virtual impactor with clean air core for the generation of aerosols with narrow
26 size distributions. *Aerosol Sci. Technol.* 18: 376-388.
- 27 Chen, B. T. (1993) Instrument calibration. In: Willeke, K.; Baron, P. A., eds. *Aerosol measurement: principles,*
28 *techniques, and applications.* New York, NY: Van Nostrand Reinhold; pp. 493-520.
- 29 Chen, B. T.; Yeh, H. C. (1987) An improved virtual impactor: design and performance. *J. Aerosol Sci.* 18: 203-214.
- 30 Chen, B. T.; Yeh, H. C.; Cheng, Y. S. (1985) A novel virtual impactor: calibration and use. *J. Aerosol Sci.* 16:
31 343-354.
- 32 Chen, B. T.; Yeh, H. C.; Cheng, Y. S. (1986) Performance of a modified virtual impactor. *Aerosol Sci. Technol.*
33 5: 369-376.
- 34 Cheng, Y.-S.; Yeh, H.-C. (1979) Particle bounce in cascade impactors. *Environ. Sci. Technol.* 13: 1392-1396.
- 35 Chow, J. C. (1995) Measurement methods to determine compliance with ambient air quality standards for suspended
36 particles. *J. Air Waste Manage. Assoc.* 45: 320-382.
- 37 Chow, J. C.; Watson, J. G. (1998) Guideline on speciated particulate monitoring (Draft 3). Research Triangle Park,
38 NC: U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards. Available:
39 <http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/driscpec.pdf> (20 March 2002).
- 40 Chow, J. C.; Watson, J. G. (1999) Ion chromatography in elemental analysis of airborne particles. In: Landsberger,
41 S.; Creatchman, M., eds. *Elemental Analysis of Airborne Particles.* Newark, NJ: Gordon and Breach Science
42 Publishers; pp. 97-137.
- 43 Chow, J. C.; Watson, J. G.; Pritchett, L. C.; Pierson, W. R.; Frazier, C. A.; Purcell, R. G. (1993) The DRI
44 thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S. air quality
45 studies. In: Lodge, J. P., Jr. *Fourth international conference on carbonaceous particles in the atmosphere;*
46 *April 1991; Vienna, Austria. Atmos. Environ. Part A* 27: 1185-1201.
- 47 Chow, J. C.; Fujita, E. M.; Watson, J. G.; Lu, Z.; Lawson, D. R.; Ashbaugh, L. L. (1994a) Evaluation of filter-based
48 aerosol measurements during the 1987 Southern California Air Quality Study. *Environ. Monit. Assess.*
49 30: 49-80.
- 50 Chow, J. C.; Watson, J. G.; Fujita, E. M.; Lu, Z.; Lawson, D. R.; Ashbaugh, L. L. (1994b) Temporal and spatial
51 variations of PM_{2.5} and PM₁₀ aerosol in the Southern California Air Quality Study. *Atmos. Environ.*
52 28: 2061-2080.
- 53 Chow, J. C.; Watson, J. G.; Lu, Z.; Lowenthal, D. H.; Frazier, C. A.; Solomon, P. A.; Thuillier, R. H.; Magliano, K.
54 (1996) Descriptive analysis of PM_{2.5} and PM₁₀ at regionally representative locations during
55 SJVAQS/AUSPEX. In: Parrish, D.; Trainer, M.; Rao, S. T.; Solomon, P. A., eds. *A&WMA international*
56 *specialty conference on regional photochemical measurements and modeling, part 2; November 1993;*
57 *San Diego, CA. Atmos. Environ.* 30: 2079-2112.

- 1 Chow, J. C.; Zielinska, B.; Watson, J. G.; Fujita, E. M.; Richards, H. W.; Neff, W. D.; Dietrich, D.; Hering, S. V.
- 2 (1998) Northern Front Range Air Quality Study. Volume A: Ambient measurements. Fort Collins, CO:
- 3 Colorado State University, Cooperative Institute for Research in the Atmosphere. Available:
- 4 <http://www.nfraqs.colostate.edu/dri.html> [4 February 2002].
- 5 Chow, J. C.; Watson, J. G.; Crow, D.; Lowenthal, D. H.; Merrifield, T. (2000) Comparison of IMPROVE and
- 6 NIOSH carbon measurements. *Aerosol Sci. Technol.* 34: 23-34.
- 7 Chow, J. C.; Watson, J. G.; Crow, D.; Lowenthal, D. H.; Merrifield, T. (2001) Comparison of IMPROVE and
- 8 NIOSH carbon measurements. *Aerosol Sci. Technol.* 34: 23-34.
- 9 Claiborn, C. S.; Finn, D.; Larson, T. V.; Koenig, J. Q. (2000) Windblown dust contributes to high PM_{2.5}
- 10 concentrations. *J. Air Waste Manage. Assoc.* 50: 1440-1445.
- 11 Clark, W. E.; Whitby, K. T. (1975) Measurements of aerosols produced by the photochemical oxidation of SO₂ in
- 12 air. *J. Colloid Interface Sci.* 51: 477-490.
- 13 Clarke, A. D. (1992) Atmospheric nuclei in the remote free-troposphere. *J. Atmos. Chem.* 14: 479-488.
- 14 Clarke, A. D.; Varner, J. L.; Eisele, F.; Mauldin, R. L.; Tanner, D.; Litchy, M. (1998) Particle production in the
- 15 remote marine atmosphere: cloud outflow and subsidence during ACE 1. *J. Geophys. Res.* A 103:
- 16 16,397-16,409.
- 17 Cobourn, W. G.; Husar, R. B.; Husar, J. D. (1978) Continuous *in situ* monitoring of ambient particulate sulfur using
- 18 flame photometry and thermal analysis. In: Husar, R. B.; Lodge, J. P., Jr.; Moore, D. J., eds. *Sulfur in the*
- 19 *atmosphere: proceedings of the international symposium; September 1977; Dubrovnik, Yugoslavia.* Atmos.
- 20 *Environ.* 12: 89-98.
- 21 Cobourn, W. G.; Husar, R. B. (1982) Diurnal and seasonal patterns of particulate sulfur and sulfuric acid in St.
- 22 Louis, July 1977-June 1978. *Atmos. Environ.* 16: 1441-1450.
- 23 Code of Federal Regulations. (2001a) Appendix J to Part 50—reference method for the determination of particulate
- 24 matter as PM₁₀ in the atmosphere. C. F. R. 40: pt. 50, app. J.
- 25 Code of Federal Regulations. (2001b) Ambient air monitoring reference and equivalent methods. C. F. R. 40: §53.
- 26 Code of Federal Regulations. (2001c) Appendix L to Part 50—reference method for the determination of fine
- 27 particulate matter as PM_{2.5} in the atmosphere. C. F. R. 40: pt. 50, app. L.
- 28 Code of Federal Regulations. (2001d) Ambient air quality surveillance. C. F. R. 40: §58.
- 29 Conner, W. D. (1966) An inertial-type particle separator for collecting large samples. *J. Air Pollut. Control Assoc.*
- 30 16: 35-38.
- 31 Conner, T. L.; Norris, G. A.; Landis, M. S.; Williams, R. W. (2001) Individual particle analysis of indoor, outdoor,
- 32 and community samples from the 1998 Baltimore particulate matter study. *Atmos. Environ.* 35: 3935-3946.
- 33 Cotham, W. E.; Bidleman, T. F. (1992) Laboratory investigations of the partitioning of organochlorine compounds
- 34 between the gas phase and atmospheric aerosols on glass fiber filters. *Environ. Sci. Technol.* 26: 469-478.
- 35 Countess, R. J. (1990) Interlaboratory analyses of carbonaceous aerosol samples. *Aerosol Sci. Technol.* 12: 114-121.
- 36 Courtney, W. J.; Shaw, R. W.; Dzubay, T. G. (1982) Precision and accuracy of a β gauge for aerosol mass
- 37 determinations. *Environ. Sci. Technol.* 16: 236-239.
- 38 Coutant, R. W.; Callahan, P. J.; Chuang, J. C.; Lewis, R. G. (1992) Efficiency of silicone-grease-coated denuders for
- 39 collection of polynuclear aromatic hydrocarbons. *Atmos. Environ. Part A* 26: 2831-2834.
- 40 Covert, D. S.; Kapustin, V. N.; Quinn, P. K.; Bates, T. S. (1992) New particle formation in the marine boundary
- 41 layer. *J. Geophys. Res. [Atmos.]* 97: 20,581-20,589.
- 42 Covert, D. S.; Wiedensohler, A.; Aalto, P.; Heintzenberg, J.; McMurry, P. H.; Leck, C. (1996) Aerosol number size
- 43 distributions from 3 to 500 nm diameter in the arctic marine boundary layer during summer and autumn.
- 44 *Tellus* 48B: 197-212.
- 45 Cui, W.; Machir, J.; Lewis, L.; Eatough, D. J.; Eatough, N. L. (1997) Fine particulate organic material at Meadview
- 46 during the project MOHAVE summer intensive study. *J. Air Waste Manage. Assoc.* 47: 357-369.
- 47 Cui, W.; Eatough, D. J.; Eatough, N. L. (1998) Fine particulate organic material in the Los Angeles Basin - I:
- 48 assessment of the high-volume Brigham Young University organic sampling system, BIG BOSS. *J. Air*
- 49 *Waste Manage. Assoc.* 48: 1024-1037.
- 50 Dagnall, R. M.; Thompson, K. C.; West, T. S. (1967) Molecular-emission in cool flames. Part I. the behaviour of
- 51 sulphur species in a hydrogen-nitrogen diffusion flame and in a shielded air-hydrogen flame. *Analyst*
- 52 92: 506-512.
- 53 Dams, R.; Robbins, J. A.; Rahn, K. A.; Winchester, J. W. (1970) Nondestructive neutron activation analysis of air
- 54 pollution particulates. *Anal. Chem.* 42: 861-867.
- 55 Dane, A. D.; Timmermans, P. A. M.; Van Sprang, H. A.; Buydens, L. M. C. (1996) A genetic algorithm for
- 56 model-free x-ray fluorescence analysis of thin film. *Anal. Chem.* 68: 2419-2425.

- 1 Davis, D. W.; Reynolds, R. L.; Tsou, G. C.; Zafonte, L. (1977) Filter attenuation corrections for x-ray fluorescence
2 analysis of atmospheric aerosols. *Anal. Chem.* 49: 1990-1993.
- 3 Davis, C. S.; Fellin, P.; Otson, R. (1987) A review of sampling methods for polyaromatic hydrocarbons in air.
4 *JAPCA* 37: 1397-1408.
- 5 DeBoer, D. K. G.; Leenaers, A. J. G.; Van Den Hoogenhof, W. W. (1995) Glancing-incidence x-ray analysis of
6 thin-layered materials: a review. *X-Ray Spectrom.* 24: 91-102.
- 7 Ding, Y.; Lee, M. L.; Eatough, D. J. (1998a) The determination of total nitrite and *N*-nitroso compounds in
8 atmospheric samples. *Int. J. Environ. Anal. Chem.* 69: 243-255.
- 9 Ding, Y.; Cui, W.; Lee, M. L.; Eatough, D. J. (1998b) Fine particulate *N*-nitroso and nitrite organic compounds in
10 the atmosphere. *Appl. Occup. Environ. Hyg.* 13: 432-438.
- 11 Ding, Y.; Koutrakis, P. (2000) Development of a dichotomous slit nozzle virtual impactor. *J. Aerosol Sci.*
12 31: 1421-1431.
- 13 Ding, Y.; Pang, Y.; Eatough, D. J.; Eatough, N. L.; Tanner, R. L. (2002) High volume diffusion denuder sampler for
14 the routine monitoring of fine particulate matter: II. field evaluation of the PC BOSS. *Aerosol Sci. Technol.*
15 36: 383-396.
- 16 Dockery, D. W.; Pope, C. A., III; Xu, X.; Spengler, J. D.; Ware, J. H.; Fay, M. E.; Ferris, B. G., Jr.; Speizer, F. E.
17 (1993) An association between air pollution and mortality in six U.S. cities. *N. Engl. J. Med.* 329: 1753-1759.
- 18 Durham, J. L.; Wilson, W. E.; Bailey, E. B. (1978) Application of an SO₂-denuder for continuous measurement of
19 sulfur in submicrometric aerosols. *Atmos. Environ.* 12: 883-886.
- 20 Dzubay, T. G. (1980) Chemical element balance method applied to dichotomous sampler data. *Ann. N. Y. Acad.*
21 *Sci.* 338: 126-144.
- 22 Dzubay, T. G.; Stevens, R. K. (1975) Ambient air analysis with dichotomous sampler and X-ray fluorescence
23 spectrometer. *Environ. Sci. Technol.* 9: 663-668.
- 24 Dzubay, T. G.; Hines, L. E.; Stevens, R. K. (1976) Particle bounce errors in cascade impactors. *Atmos. Environ.*
25 10: 229-234.
- 26 Dzubay, T. G.; Stevens, R. K.; Peterson, C. M. (1977) Application of the dichotomous sampler to the
27 characterization of ambient aerosols. In: Dzubay, T. G., ed. *X-ray fluorescence analysis of environmental*
28 *samples.* Ann Arbor, MI: Ann Arbor Science Publishers, Inc.
- 29 Easter, R. C.; Peters, L. K. (1994) Binary homogeneous nucleation: temperature and relative humidity fluctuations,
30 nonlinearity, and aspects of new particle production in the atmosphere. *J. Appl. Meteorol.* 33: 775-784.
- 31 Eatough, D. J. (1999) BOSS, the Brigham Young University Organic Sampling System: determination of particulate
32 carbonaceous material using diffusion denuder sampling technology. In: Lane, D., ed. *Gas and particle phase*
33 *measurements of atmospheric organic compounds.* New York, NY: Gordon and Breach Science Publishers.
34 (Advances in environmental, industrial and process control technologies: v. 2).
- 35 Eatough, D. J.; Wadsworth, A.; Eatough, D. A.; Crawford, J. W.; Hansen, L. D.; Lewis, E. A. (1993) A
36 multiple-system, multi-channel diffusion denuder sampler for the determination of fine-particulate organic
37 material in the atmosphere. *Atmos. Environ. Part A* 27: 1213-1219.
- 38 Eatough, D. J.; Tang, H.; Cui, W.; Machir, J. (1995) Determination of the size distribution and chemical composition
39 of fine particulate semi-volatile organic material in urban environments using diffusion denuder technology.
40 In: Phalen, R. F.; Bates, D. V., eds. *Proceedings of the colloquium on particulate air pollution and human*
41 *mortality and morbidity, part II; January 1994; Irvine, CA.* *Inhalation Toxicol.* 7: 691-710.
- 42 Eatough, D. J.; Eatough, D. A.; Lewis, L.; Lewis, E. A. (1996) Fine particulate chemical composition and light
43 extinction at Canyonlands National Park using organic particulate material concentrations obtained with a
44 multisystem, multichannel diffusion denuder sampler. *J. Geophys. Res. [Atmos.]* 101: 19,515-19,531.
- 45 Eatough, D. J.; Obeidi, F.; Pang, Y.; Ding, Y.; Eatough, N. L.; Wilson, W. E. (1999a) Integrated and real-time
46 diffusion denuder sampler for PM_{2.5}. *Atmos. Environ.* 33: 2835-2844.
- 47 Eatough, D. J.; Pang, Y.; Eatough, N. L. (1999b) Determination of PM_{2.5}, sulfate and nitrate with a PC-BOSS
48 designed for routine sampling for semi-volatile particulate matter. *J. Air Waste Manage. Assoc.* 49(special
49 issue): PM69-75.
- 50 Eatough, D. J.; Eatough, N. L.; Obeidi, F.; Pang, Y.; Modey, W.; Long, R. (2001) Continuous determination of
51 PM_{2.5} mass, including semi-volatile species. *Aerosol Sci. Technol.* 34: 1-8.
- 52 Fairchild, C. I.; Wheat, L. D. (1984) Calibration and evaluation of a real-time cascade impactor. *Am. Ind. Hyg.*
53 *Assoc. J.* 45: 205-211.
- 54 Falconer, R. L.; Bidleman, T. F.; Cotham, W. E. (1995) Preferential sorption of non- and
55 mono-ortho-polychlorinated biphenyls to urban aerosols. *Environ. Sci. Technol.* 29: 1666-1673.

- 1 Fang, C. P.; McMurry, P. H.; Marple, V. A.; Rubow, K. L. (1991) Effect of flow-induced relative humidity changes
2 on size cuts for sulfuric acid droplets in the microorifice uniform deposit impactor (MOUDI). *Aerosol Sci.*
3 *Technol.* 14: 266-277.
- 4 Farwell, S. O.; Rasmussen, R. A. (1976) Limitations of the FPD and ECD in atmospheric analysis: a review. *J.*
5 *Chromatogr. Sci.* 14: 224-234.
- 6 Fassel, V. A.; Kniseley, R. N. (1974) Inductively coupled plasma-optical emission spectroscopy. *Anal. Chem.*
7 46: 1110A-1120A.
- 8 Federal Register. (1987) Revisions to the national ambient air quality standards for particulate matter. F. R. (July 1)
9 52: 24,634-24,669.
- 10 Federal Register. (1997) National ambient air quality standards for particulate matter; final rule. F. R. (July 18)
11 62: 38,652-38,752.
- 12 Federal Register. (1998) National ambient air quality standards for particulate matter and revised requirements for
13 designation of reference and equivalent methods for PM_{2.5} and ambient air quality surveillance for particulate
14 matter; correction. F. R. (February 17) 63: 7710-7718.
- 15 Fergenson, D. P.; Song, X.-H.; Ramadan, Z.; Allen, J. O.; Hughes, L. S.; Cass, G. R.; Hopke, P. K.; Prather, K. A.
16 (2001) Quantification of ATOFMS data by multivariate methods. *Anal. Chem.* 73: 3535-3541.
- 17 Fernandez, F. J. (1989) Atomic absorption spectroscopy. In: Lodge, J. P., Jr., ed. *Methods of Air Sampling and*
18 *Analysis*. 3rd ed. Chelsea, MI: Lewis Publishers, Inc.; pp. 83-89.
- 19 Finn, D.; Rumburg, B.; Claiborn, C.; Barnesberger, L.; Siems, W. F.; Koenig, J.; Larson, T.; Norris, G. (2001)
20 Sampling artifacts from the use of denuder tubes with glycerol based coatings in the measurement of
21 atmospheric particulate matter. *Environ. Sci. Technol.* 35: 40-44.
- 22 Fitz, D. R. (1990) Reduction of the positive organic artifact on quartz filters. *Aerosol. Sci. Technol.* 12: 142-148.
- 23 Flocchini, R. G.; Cahill, T. A.; Shadoan, D. J.; Lange, S. J.; Eldred, R. A.; Feeney, P. J.; Wolfe, G. W.; Simmeroth,
24 D. C.; Suder, J. K. (1976) Monitoring California's aerosols by size and elemental composition. *Environ. Sci.*
25 *Technol.* 10: 76-82.
- 26 Forney, L. J.; Ravenhall, D. G.; Winn, D. S. (1978) Aerosol impactors: a study of a fluid jet impinging upon a void.
27 *J. Appl. Phys.* 49: 2339-2345.
- 28 Forney, L. J.; Ravenhall, D. G.; Lee, S. S. (1982) Experimental and theoretical study of a two-dimensional virtual
29 impactor. *Environ. Sci. Technol.* 16: 492-497.
- 30 Friedlander, S. K. (1970) The characterization of aerosols distributed with respect to size and chemical composition.
31 *J. Aerosol Sci.* 1: 295-307.
- 32 Friedlander, S. K. (1977) *Smoke, dust and haze: fundamentals of aerosol behavior*. New York, NY: John Wiley &
33 Sons.
- 34 Friedlander, S. K.; Yeh, E. K. (1998) The submicron atmospheric aerosol as a carrier of reactive chemical species:
35 case of peroxides. *Appl. Occup. Environ. Hyg.* 13: 416-420.
- 36 Friedlander, S. K. (2000). *Smoke, dust and haze: fundamentals of aerosol dynamics*. 2nd ed. New York, NY:
37 Oxford University Press.
- 38 Fuchs, N. A. (1964) *The mechanics of aerosols*. New York, NY: Pergamon Press.
- 39 Fuchs, N. A. (1989) *The mechanics of aerosols*. New York, NY: Dover Publications.
- 40 Fung, K. (1990) Particulate carbon speciation by MnO₂ oxidation. *Aerosol Sci. Technol.* 12: 122-127.
- 41 Fung, K.; Chow, J. C.; Watson, J. G. (2002) Evaluation of OC/EC speciation by thermal manganese dioxide
42 oxidation and the IMPROVE method. *J. Air Waste Manage. Assoc.* 52: 1333-1341.
- 43 Gallorini, M. (1995) Trace element monitoring in atmospheric pollution processes by neutron activation analysis.
44 *Microchem. J.* 51: 127-137.
- 45 Gard, E.; Mayer, J. E.; Morrical, B. D.; Dienes, T.; Fergenson, D. P.; Prather, K. A. (1997) Real-time analysis of
46 individual atmospheric aerosol particles: design and performance of a portable ATOFMS. *Anal. Chem.*
47 69: 4083-4091.
- 48 Gauderman, W. J.; McConnell, R.; Gilliland, F.; London, S.; Thomas, D.; Avol, E.; Vora, H.; Berhane, K.;
49 Rappaport, E. B.; Lurmann, F.; Margolis, H. G.; Peters, J. (2000) Association between air pollution and lung
50 function growth in southern California children. *Am. J. Respir. Crit. Care Med.* 162: 1383-1390.
- 51 Ge, Z.; Wexler, A. S.; Johnston, M. V. (1998) Laser desorption/ionization of single ultrafine multicomponent
52 aerosols. *Environ. Sci. Technol.* 32: 3218-3223.
- 53 Geller, M. D.; Kim, S.; Misra, C.; Sioutas, C.; Olson, B. A.; Marple, V. A. (2002) Methodology for measuring
54 size-dependent chemical composition of ultrafine particles. *Aerosol Sci. Technol.* 36: 748-763.
- 55 Gong, H., Jr.; Linn, W. S.; Sioutas, C.; Terrell, S. L.; Clark, K. W.; Anderson, K. R.; Terrell, L. (2003) Controlled
56 exposures of healthy and asthmatic volunteers to concentrated ambient fine particles in Los Angeles.
57 *Inhalation Toxicol.* 15: 305-325.

- 1 Goss, K.-U.; Eisenreich, S. J. (1997) Sorption of volatile organic compounds to particles from a combustion source
2 at different temperatures and relative humidities. *Atmos. Environ.* 31: 2827-2834.
- 3 Gray, A. L.; Williams, J. G. (1987a) Oxide and doubly charged ion response of a commercial inductively coupled
4 plasma mass spectrometry instrument. *J. Anal. At. Spectrom.* 2: 81-82.
- 5 Gray, A. L.; Williams, J. G. (1987b) System optimisation and the effect on polyatomic, oxide and doubly charged
6 ion response of a commercial inductively coupled plasma mass spectrometry instrument. *J. Anal. At.*
7 *Spectrom.* 2: 599-606.
- 8 Grosjean, D. (1983) Polycyclic aromatic hydrocarbons in Los Angeles air from samples collected on Teflon, glass
9 and quartz filters. *Atmos. Environ.* 17: 2565-2573.
- 10 Grosjean, D.; Parmar, S. S. (1990) Interferences from aldehydes and peroxyacetyl nitrate when sampling urban air
11 organic acids on alkaline traps. *Environ. Sci. Technol.* 24: 1021-1026.
- 12 Grosjean, D.; Williams, E. L., II; Grosjean, E.; Novakov, T. (1994) Evolved gas analysis of secondary organic
13 aerosols. *Aerosol Sci. Technol.* 21: 306-324.
- 14 Gundel, L. A.; Lane, D. A. (1999) Sorbent-coated diffusion denuders for direct measurement of gas/particle
15 partitioning by semi-volatile organic compounds. In: Lane, D. A., ed. *Gas and particle phase measurements of*
16 *atmospheric organic compounds*. Amsterdam, The Netherlands: Gordon and Breach Science Publishers.
17 (Advances in environmental, industrial and process control technologies: v. 2).
- 18 Gundel, L. A.; Lee, V. C.; Mahanama, K. R. R.; Stevens, R. K.; Daisey, J. M. (1995) Direct determination of the
19 phase distributions of semi-volatile polycyclic aromatic hydrocarbons using annular denuders. *Atmos.*
20 *Environ.* 29: 1719-1733.
- 21 Hänninen, O. O.; Koistinen, K. J.; Kousa, A.; Keski-Karhu, J.; Jantunen, M. J. (2002) Quantitative analysis of
22 environmental factors in differential weighing of blank teflon filters. *J. Air Waste Manage. Assoc.*
23 52: 134-139.
- 24 Hansen, A. D. A.; McMurry, P. H. (1990) An intercomparison of measurements of aerosol elemental carbon during
25 the 1986 carbonaceous species method comparison study. *J. Air Waste Manage. Assoc.* 40: 894-895.
- 26 Hansen, A. D. A.; Rosen, H.; Novakov, T. (1984) The aethalometer - an instrument for the real-time measurement of
27 optical absorption by aerosol particles. *Sci. Total Environ.* 36: 191-196.
- 28 Harman, J. N. (1989) Inductively coupled plasma emission spectroscopy. In: Lodge, J. P., Jr., ed. *Methods of air*
29 *sampling and analysis*. 3rd ed. Chelsea, MI: Lewis Publishers, Inc.; pp. 89-92.
- 30 Haupt, O.; Klane, B.; Schaefer, C.; Dannecker, W. (1995) Preparation of quartz fibre filter standards for x-ray
31 fluorescence analysis of aerosol samples. *X-Ray Spectrom.* 24: 267-275.
- 32 He, K.; Yang, F.; Ma, Y.; Zhang, Q.; Yao, X.; Chan, C. K.; Cadle, S.; Chan, T.; Mulawa, P. (2001) The
33 characteristics of PM_{2.5} in Beijing, China. *Atmos. Environ.* 35: 4959-4970.
- 34 Hegg, D. A.; Radke, L. F.; Hobbs, P. V. (1990) Particle production associated with marine clouds. *J. Geophys. Res.*
35 [Atmos.] 95: 13,917-13,926.
- 36 Hegg, D. A.; Radke, L. F.; Hobbs, P. V. (1991) Measurements of Aitken nuclei and cloud condensation nuclei in the
37 marine atmosphere and their relation to the DMS-cloud-climate hypothesis. *J. Geophys. Res.* [Atmos.]
38 96: 18,727-18,733.
- 39 Hering, S.; Cass, G. (1999) The magnitude of bias in the measurement of PM_{2.5} arising from volatilization of
40 particulate nitrate from Teflon filters. *J. Air Waste Manage. Assoc.* 49: 725-733.
- 41 Hering, S. V.; Appel, B. R.; Cheng, W.; Salaymeh, F.; Cadle, S. H.; Mulawa, P. A.; Cahill, T. A.; Eldred, R. A.;
42 Surovik, M.; Fitz, D.; Howes, J. E.; Knapp, K. T.; Stockburger, L.; Turpin, B. J.; Huntzicker, J. J.; Zhang,
43 X.-Q.; McMurry, P. H. (1990) Comparison of sampling methods for carbonaceous aerosols in ambient air.
44 *Aerosol Sci. Technol.* 12: 200-213.
- 45 Hinds, W. C. (1999) *Aerosol technology: properties, behavior, and measurement of airborne particles*. 2nd ed.
46 New York, NY: John Wiley & Sons.
- 47 Hinz, K.-P.; Kaufmann, R.; Spengler, B. (1994) Laser-induced mass analysis of single particles in the airborne state.
48 *Anal. Chem.* 66: 2071-2076.
- 49 Hitzenberger, R.; Dusek, U.; Berner, A. (1996) Black carbon measurements using an integrating sphere. *J. Geophys.*
50 *Res.* [Atmos.] 101: 19,601-19,606.
- 51 Hitzenberger, R.; Berner, A.; Dusek, U.; Alabashi, R. (1997) Humidity-dependent growth of size-segregated aerosol
52 samples. *Aerosol Sci. Technol.* 27: 116-130.
- 53 Hitzenberger, R.; Jennings, S. G.; Larson, S. M.; Dillner, A.; Cachier, H.; Galambos, Z.; Rouc, A.; Spain, T. G.
54 (1999) Intercomparison of measurement methods for black carbon aerosols. *Atmos. Environ.* 33: 2823-2833.
- 55 Holyńska, B.; Ptasinski, J.; Maenhaut, W.; Annegarn, H. J. (1997) Energy-dispersive x-ray fluorescence
56 spectrometer with capillary optics for the chemical analysis of atmospheric aerosols with high time resolution.
57 *J. Aerosol Sci.* 28: 1455-1463.

- 1 Hoppel, W. A.; Frick, G. M.; Fitzgerald, J. W.; Larson, R. E. (1994) Marine boundary layer measurements of new
2 particle formation and the effects nonprecipitating clouds have on aerosol size distribution. *J. Geophys. Res.*
3 [*Atmos.*] 99: 14,443-14,459.
- 4 Houck, J. E.; Chow, J. C.; Watson, J. G.; Simons, C. A.; Pritchett, L. C.; Goulet, J. M.; Frazier, C. A. (1989)
5 Determination of particle size distribution and chemical composition of particulate matter from selected
6 sources in California: volume I and executive summary (final report). Sacramento, CA: California Air
7 Resources Board.
- 8 Hounam, R. F.; Sherwood, R. J. (1965) The cascade centripeter: a device for determining the concentration and size
9 distribution of aerosols. *Am. Ind. Hyg. Assoc. J.* 26: 122-131.
- 10 Huntzicker, J. J.; Hoffman, R. S.; Ling, C.-S. (1978) Continuous measurement and speciation of sulfur-containing
11 aerosols by flame photometry. *Atmos. Environ.* 12: 83-88.
- 12 Huntzicker, J. J.; Johnson, R. L.; Shah, J. J.; Cary, R. A. (1982) Analysis of organic and elemental carbon in ambient
13 aerosols by a thermal-optical method. In: Wolff, G. T.; Klimisch, R. L., eds. *Particulate carbon - atmospheric*
14 *life cycle: proceedings of an international symposium; October 1980; Warren, MI.* New York, NY: Plenum
15 Press; pp. 79-88.
- 16 Husar, R. B.; Tratt, D. M.; Schichtel, B. A.; Falke, S. R.; Li, F.; Jaffe, D.; Gassó, S.; Gill, T.; Laulainen, N. S.; Lu,
17 F.; Reheis, M. C.; Chun, Y.; Westphal, D.; Holben, B. N.; Gueymard, C.; McKendry, I.; Kuring, N.;
18 Feldman, G. C.; McClain, C.; Frouin, R. J.; Merrill, J.; DuBois, D.; Vignola, F.; Murayama, T.; Nickovic, S.;
19 Wilson, W. E.; Sassen, K.; Sugimoto, N.; Malm, W. C. (2001) The Asian dust events of April 1998. *J.*
20 *Geophys. Res.* 106: 18,317-18,330.
- 21 Jackson, K. W.; Mahmood, T. M. (1994) Atomic absorption, atomic emission, and flame emission spectrometry.
22 *Anal. Chem.* 66: 252R-279R.
- 23 Jaklevic, J. M.; Loo, B. W.; Goulding, F. S. (1977) Photon-induced X-ray fluorescence analysis using
24 energy-dispersive detector and dichotomous sampler. In: Dzubay, T. G., ed. *X-ray fluorescence analysis of*
25 *environmental samples.* Ann Arbor, MI: Ann Arbor Science Publishers, Inc.; pp. 3-18.
- 26 Jaklevic, J. M.; Gatti, R. C.; Goulding, F. S.; Loo, B. W. (1981a) A β -gauge method applied to aerosol samples.
27 *Environ. Sci. Technol.* 15: 680-686.
- 28 Jaklevic, J. M.; Loo, B. W.; Fujita, T. Y. (1981b) Automatic particulate sulfur measurements with a dichotomous
29 sampler and on-line x-ray fluorescence analysis. *Environ. Sci. Technol.* 15: 687-690.
- 30 Jang, M.; Kamens, R. M. (1998) A thermodynamic approach for modeling partitioning of semivolatile organic
31 compounds on atmospheric particulate matter: humidity effects. *Environ. Sci. Technol.* 32: 1237-1243.
- 32 Jang, M.; Kamens, R. M. (1999) Exploratory model approach for adsorption partitioning of SOCs on inorganic
33 particles. *Environ. Sci. Technol.*
- 34 Jang, M.; Kamens, R. M.; Leach, K. B.; Strommen, M. R. (1997) A thermodynamic approach using group
35 contribution methods to model the partitioning of semivolatile organic compounds on atmospheric particulate
36 matter. *Environ. Sci. Technol.* 31: 2805-2811.
- 37 Jenkins, B. M.; Jones, A. D.; Turn, S. Q.; Williams, R. B. (1996) Particle concentrations, gas-particle partitioning,
38 and species intercorrelations for polycyclic aromatic hydrocarbons (PAH) emitted during biomass burning.
39 *Atmos. Environ.* 30: 3825-3835.
- 40 Johansson, T. B.; Askelsson, R.; Johansson, S. A. E. (1970) X-ray analysis: elemental trace analysis at the 10^{-12} g
41 level. *Nucl. Instrum. Methods* 84: 141-143.
- 42 John, W.; Sethi, V. (1993) Threshold for resuspension by particle impaction. *Aerosol Sci. Technol.* 19: 69-79.
- 43 John, W.; Wall, S. M.; Ondo, J. L. (1988) A new method for nitric acid and nitrate aerosol measurement using the
44 dichotomous sampler. *Atmos. Environ.* 22: 1627-1635.
- 45 Johnson, M V.; Wexler, A. S. (1995) MS of individual aerosol particles. *Anal. Chem.* 67: 721A-726A.
- 46 Johnson, R. L.; Shah, J. J.; Huntzicker, J. J. (1980) Analysis of organic, elemental, and carbonate carbon in ambient
47 aerosols. In: Verner, S. S. *Sampling and analysis of toxic organics in the atmosphere: proceedings of a*
48 *symposium; August, 1979; Boulder, CO.* Philadelphia, PA: American Society for Testing and Materials,
49 pp. 111-119. [ASTM Special Technical Publication 721].
- 50 Kamens, R. M.; Coe, D. L. (1997) A large gas-phase stripping device to investigate rates of PAH evaporation from
51 airborne diesel soot particles. *Environ. Sci. Technol.* 31: 1830-1833.
- 52 Kamens, R. M.; Jaoui, M. (2001) Modeling aerosol formation from α -pinene + NO_x in the presence of natural
53 sunlight using gas phase kinetics and gas-particle partitioning theory. *Environ. Sci. Technol.* 35: 1394-1405.
- 54 Kamens, R.; Odum, J.; Fan, Z.-H. (1995) Some observations on times to equilibrium for semivolatile polycyclic
55 aromatic hydrocarbons. *Environ. Sci. Technol.* 29: 43-50.
- 56 Kamens, R.; Jang, M.; Chien, C.-J.; Leach, K. (1999) Aerosol formation from the reaction of α -pinene and ozone
57 using a gas-phase kinetics-aerosol partitioning model. *Environ. Sci. Technol.* 33: 1430-1438.

- 1 Kao, A. S.; Friedlander, S. K. (1995) Frequency distributions of PM_{10} chemical components and their sources.
- 2 Environ. Sci. Technol. 29: 19-28.
- 3 Kavouras, I. G.; Koutrakis, P. (2001) Use of polyurethane foam as the impaction substrate/collection medium in
- 4 conventional inertial impactors. Aerosol Sci. Technol. 34: 46-56.
- 5 Keeler, G. J.; Brachaczek, W. W.; Gorse, R. A., Jr.; Japar, S. M.; Pierson, W. R. (1988) Effect of ambient humidity
- 6 on dichotomous sampler coarse/fine ratios. Atmos. Environ. 22: 1715-1720.
- 7 Keeler, G. J.; Pirrone, N. (1996) Atmospheric transport and deposition of trace elements to Lake Erie from urban
- 8 areas. Water Sci. Technol. 33: 259-265.
- 9 Kegler, S. R.; Wilson, W. E.; Marcus, A. H. (2001) PM_{10} , intermodal ($PM_{2.5-10}$) mass, and the soil component of
- 10 $PM_{2.5}$ in Phoenix, AZ, 1995-96. Aerosol Sci. Technol. 35: 914-920.
- 11 Keywood, M. D.; Ayers, G. P.; Gras, J. L.; Gillett, R. W.; Cohen, D. D. (1999) Relationships between size
- 12 segregated mass concentration data and ultrafine particle number concentrations in urban areas. Atmos.
- 13 Environ. 33: 2907-2913.
- 14 Keywood, M. D.; Ayers, G. P.; Gras, J. L.; Gillett, R. W.; Cohen, D. D. (2000) Size distribution and sources of
- 15 aerosol in Launceston, Australia, during winter 1997. J. Air Waste Manage. Assoc. 50: 418-427.
- 16 Khlystov, A.; Wyers, G. P.; Slanina, J. (1995) The steam-jet aerosol collector. Atmos. Environ. 29: 2229-2234.
- 17 Kim, Y. J.; Boatman, J. F.; Gunter, R. L.; Wellman, D. L.; Wilkison, S. W. (1993) Vertical distribution of
- 18 atmospheric aerosol size distribution over south-central New Mexico. Atmos. Environ. Part A 27: 1351-1362.
- 19 Kim, B. M.; Lester, J.; Tisopulos, L.; Zeldin, M. D. (1999) Nitrate artifacts during $PM_{2.5}$ sampling in the South Coast
- 20 Air Basin of California. J. Air Waste Manage. Assoc. 49(special issue): PM142-153.
- 21 Kim, B. M.; Cassmassi, J.; Hogo, H.; Zeldin, M. D. (2001a) Positive organic carbon artifacts on filter medium
- 22 during $PM_{2.5}$ sampling in the South Coast Air Basin. Aerosol Sci. Technol. 34: 35-41.
- 23 Kim, S.; Jaques, P. A.; Chang, M. C.; Froines, J. R.; Sioutas, C. (2001b) Versatile aerosol concentration enrichment
- 24 system (VACES) for simultaneous in vivo and in vitro evaluation of toxic effects of ultrafine, fine and coarse
- 25 ambient particles Part I: development and laboratory characterization. J. Aerosol Sci. 32: 1281-1297.
- 26 Kim, S.; Jaques, P. A.; Chang, M. C.; Barone, T.; Xiong, C.; Friedlander, S. K.; Sioutas, C. (2001c) Versatile
- 27 aerosol concentration enrichment system (VACES) for simultaneous in vivo and in vitro evaluation of toxic
- 28 effects of ultrafine, fine and coarse ambient particles Part II: field evaluation. J. Aerosol Sci. 32: 1299-1314.
- 29 Kirchstetter, T. W.; Corrigan, C. E.; Novakov, T. (2001) Laboratory and field investigation of the adsorption of
- 30 gaseous organic compounds onto quartz filters. Atmos. Environ. 35: 1663-1671.
- 31 Kittelson, D. B. (1998) Engines and nanoparticles: a review. J. Aerosol Sci. 29: 575-588.
- 32 Kittelson, D. B.; McKenzie, R.; Vermeersch, M.; Dorman, F.; Pui, D.; Linne, M.; Liu, B.; Whitby, K. (1978) Total
- 33 sulfur aerosol concentration with an electrostatically pulsed flame photometric detector system. Atmos.
- 34 Environ. 12: 105-111.
- 35 Klouda, G. A.; Klinedinst, D. B.; Steel, E. B.; Benner, B. A., Jr.; Parish, H. J. (1996) Exploring a method to produce
- 36 an urban dust particle filter standard. J. Aerosol Sci. 27(suppl. 1): S351-S352.
- 37 Koistinen, K. J.; Kousa, A.; Tenhola, V.; Hänninen, O.; Jantunen, M. J.; Oglesby, L.; Kuenzli, N.; Georgoulis, L.
- 38 (1999) Fine particle ($PM_{2.5}$) measurement methodology, quality assurance procedures and pilot results of the
- 39 EXPOLIS study. J. Air Waste Manage. Assoc. 49: 1212-1220.
- 40 Korhonen, P.; Kulmala, M.; Laaksonen, A.; Viisanen, Y.; McGraw, R.; Seinfeld, J. H. (1999) Ternary nucleation of
- 41 H_2SO_4 , NH_3 , and H_2O in the atmosphere. J. Geophys. Res. 104: 26,349-26,353.
- 42 Koutrakis, P.; Kelly, B. P. (1993) Equilibrium size of atmospheric aerosol sulfates as a function of particle acidity
- 43 and ambient relative humidity. J. Geophys. Res. [Atmos.] 98: 7141-7147.
- 44 Koutrakis, P.; Wolfson, J. M.; Slater, J. L.; Brauer, M.; Spengler, J. D.; Stevens, R. K.; Stone, C. L. (1988a)
- 45 Evaluation of an annular denuder/filter pack system to collect acidic aerosols and gases. Environ. Sci.
- 46 Technol. 22: 1463-1468.
- 47 Koutrakis, P.; Wolfson, J. M.; Spengler, J. D. (1988b) An improved method for measuring aerosol strong acidity:
- 48 results from a nine-month study in St. Louis, Missouri and Kingston, Tennessee. Atmos. Environ.
- 49 22: 157-162.
- 50 Koutrakis, P.; Wolfson, J. M.; Spengler, J. D.; Stern, B.; Franklin, C. A. (1989) Equilibrium size of atmospheric
- 51 aerosol sulfates as a function of the relative humidity. J. Geophys. Res. [Atmos.] 94: 6442-6448.
- 52 Koutrakis, P.; Thompson, K. M.; Wolfson, J. M.; Spengler, J. D.; Keeler, G. J.; Slater, J. L. (1992) Determination of
- 53 aerosol strong acidity losses due to interactions of collected particles: results from laboratory and field
- 54 studies. Atmos. Environ. Part A 26: 987-995.
- 55 Koutrakis, P.; Sioutas, C.; Ferguson, S. T.; Wolfson, J. M.; Mulik, J. D.; Burton, R. M. (1993) Development and
- 56 evaluation of a glass honeycomb denuder/filter pack system to collect atmospheric gases and particles.
- 57 Environ. Sci. Technol. 27: 2497-2501.

- 1 Koutrakis, P.; Wang, P.-Y.; Wolfson, J. M.; Sioutas, C., inventors. (1996) Method and apparatus to measure
2 particulate matter in gas. U.S. patent 5,571,945. November 5. Available: www.patents.ibm.com [1999,
3 November 24].
- 4 Krieger, M. S.; Hites, R. A. (1992) Diffusion denuder for the collection of semivolatile organic compounds. *Environ.*
5 *Sci. Technol.* 26: 1551-1555.
- 6 Kulmala, M.; Toivonen, A.; Mäkelä, J. M.; Laaksonen, A. (1998) Analysis of the growth of nucleation mode
7 particles observed in Boreal forest. *Tellus* 50B: 449-462.
- 8 Kulmala, M.; Pirjola, L.; Mäkelä, J. M. (2000) Stable sulphate clusters as a source of new atmospheric particles.
9 *Nature* (London, U. K.) 404: 66-69.
- 10 Kusko, B. H.; Cahill, T. A.; Eldred, R. A.; Matsuda, Y.; Miyake, H. (1989) Nondestructive analysis of total
11 nonvolatile carbon by Forward Alpha Scattering Technique (FAST). *Aerosol Sci. Technol.* 10: 390-396.
- 12 Lammel, G.; Novakov, T. (1995) Water nucleation properties of carbon black and diesel soot particles. *Atmos.*
13 *Environ.* 29: 813-823.
- 14 Landsberger, S. (1988) Improved methodology for the determination of the seven elemental tracer long-distance
15 pollution signatures using thermal and epithermal neutron activation analysis. *Anal. Chem.* 60: 1842-1845.
- 16 Landsberger, S.; Wu, D. (1993) Improvement of analytical sensitivities for the determination of antimony, arsenic,
17 cadmium, indium, iodine, molybdenum, silicon and uranium in airborne particulate matter by epithermal
18 neutron activation analysis. *J. Radioanal. Nucl. Chem.* 167: 219-225.
- 19 Landsberger, S.; Wu, D.; Vermette, S. J.; Cizek, W. (1997) Intercomparison of IAEA airborne particulate matter
20 reference material. *J. Radioanal. Nucl. Chem.* 215: 117-127.
- 21 Lane, D. A.; Johnson, N. D.; Barton, S. C.; Thomas, G. H. S.; Schroeder, W. H. (1988) Development and evaluation
22 of a novel gas and particle sampler for semivolatile chlorinated organic compounds in ambient air. *Environ.*
23 *Sci. Technol.* 22: 941-947.
- 24 Lavanchy, V. M. H.; Gäggeler, H. W.; Nyeki, S.; Baltensperger, U. (1999) Elemental carbon (EC) and black carbon
25 (BC) measurements with a thermal method and an aethalometer at the high-alpine research station
26 Jungfraujoch. *Atmos. Environ.* 33: 2759-2769.
- 27 Lawless, P. A.; Rodes, C. E.; Evans, G.; Sheldon, L.; Creason, J. (2001) Aerosol concentrations during the 1999
28 Fresno Exposure Studies as functions of size, season and meteorology. *Aerosol Sci. Technol.* 34: 66-74.
- 29 Lawrence, J. E.; Koutrakis, P. (1994) Measurement of atmospheric formic and acetic acids: methods evaluation and
30 results from field studies. *Environ. Sci. Technol.* 28: 957-964.
- 31 Lawrence, J.; Koutrakis, P. (1996a) Measurement and speciation of gas and particulate phase organic acidity in an
32 urban environment: 1. analytical. *J. Geophys. Res. [Atmos.]* 101: 9159-9169.
- 33 Lawrence, J.; Koutrakis, P. (1996b) Measurement and speciation of gas and particulate phase organic acidity in an
34 urban environment: 2. speciation. *J. Geophys. Res. [Atmos.]* 101: 9171-9184.
- 35 Lawson, D. R. (1990) The Southern California Air Quality Study. *J. Air Waste Manage. Assoc.* 40: 156-165.
- 36 Leach, K. B.; Kamens, R. M.; Strommen, M. R.; Jang, M. (1999) Partitioning of semivolatile organic compounds in
37 the presence of a secondary organic aerosol in a controlled atmosphere. *J. Atmos. Chem.* 33: 241-264.
- 38 Lee, W.-M. G.; Shih, P.-M.; Wang, C.-S. (1997) The influence of relative humidity on the size of atmospheric
39 aerosol. *J. Environ. Sci. Health Part A: Environ. Sci. Eng. Toxic Hazard. Subst. Control* 32: 1085-1097.
- 40 Lewis, C. W.; Macias, E. S. (1980) Composition of size-fractionated aerosol in Charleston, West Virginia. *Atmos.*
41 *Environ.* 14: 185-194.
- 42 Lewtas, J.; Pang, Y.; Booth, D.; Reimer, S.; Eatough, D. J.; Gundel, L. A. (2001) Comparison of sampling methods
43 for semi-volatile organic carbon associated with PM_{2.5}. *Aerosol Sci. Technol.* 34: 9-22.
- 44 Li, W.; Montassier, N.; Hopke, P. K. (1992) A system to measure the hygroscopicity of aerosol particles. *Aerosol*
45 *Sci. Technol.* 17: 25-35.
- 46 Li, N.; Kim, S.; Wang, M.; Froines, J. R.; Sioutas, C.; Nel, A. (2002) Use of a stratified oxidative stress model to
47 study the biological effects of ambient concentrated and diesel exhaust particulate matter. *Inhalation Toxicol.*
48 14: 459-486.
- 49 Li, N.; Sioutas, C.; Froines, J. R.; Cho, A.; Misra, C.; Nel, A. (2003) Ultrafine particulate pollutants induce oxidative
50 stress and mitochondrial damage. *Environ. Health Perspect.* 111: 455-460.
- 51 Liang, Z.; Chan, C. K. (1997) A fast technique for measuring water activity of atmospheric aerosols. *Aerosol Sci.*
52 *Technol.* 26: 255-268.
- 53 Liang, C.; Pankow, J. F.; Odum, J. R.; Seinfeld, J. H. (1997) Gas/particle partitioning of semivolatile organic
54 compounds to model inorganic, organic, and ambient smog aerosols. *Environ. Sci. Technol.* 31: 3086-3092.
- 55 Lin, J. J.; Noll, K. E.; Holsen, T. M. (1994) Dry deposition velocities as a function of particle size in the ambient
56 atmosphere. *Aerosol Sci. Technol.* 20: 239-252.

- 1 Lindskog, A.; Brorström-Lundén, E.; Alfheim, I.; Hagen, I. (1987) Chemical transformation of PAH on airborne
2 particles by exposure to NO₂ during sampling: a comparison between two filter media. *Sci. Total Environ.*
3 61: 51-57.
- 4 Lioussé, C.; Cachier, H.; Jennings, S. G. (1993) Optical and thermal measurements of black carbon aerosol content
5 in different environments: variation of the specific attenuation cross-section, sigma σ . *Atmos. Environ. Part A*
6 27: 1203-1211.
- 7 Long, R. W.; Smith, R.; Smith, S.; Eatough, N. L.; Mangelson, N. F.; Eatough, D. J.; Pope, C. A., III; Wilson, W. E.
8 (2002) Sources of fine particulate material along the Wasatch Front. *Ener. Fuels* 16: 282-293.
- 9 Loo, B. W.; Cork, C. P. (1988) Development of high efficiency virtual impactors. *Aerosol Sci. Technol.* 9: 167-176.
- 10 Loo, B. W.; Jaklevic, J. M.; Goulding, F. S. (1976) Dichotomous virtual impactors for large scale monitoring of
11 airborne particulate matter. In: Liu, B. Y. H., ed. *Fine particles: aerosol generation, measurement, sampling,*
12 *and analysis.* New York, NY: Academic Press; pp. 311-350.
- 13 Loo, B. W.; French, W. R.; Gatti, R. C.; Goulding, F. S.; Jaklevic, J. M.; Llacer, J.; Thompson, A. C. (1978)
14 Large-scale measurement of airborne particulate sulfur. *Atmos. Environ.* 12: 759-771.
- 15 Lundgren, D. A.; Burton, R. M. (1995) Effect of particle size distribution on the cut point between fine and coarse
16 ambient mass fractions. In: Phalen, R. F.; Bates, D. V., eds. *Proceedings of the colloquium on particulate air*
17 *pollution and human mortality and morbidity; January 1994; Irvine, CA.* *Inhalation Toxicol.* 7: 131-148.
- 18 Lundgren, D. A.; Hausknecht, B. J.; Burton, R. M. (1984) Large particle size distribution in five U.S. cities and the
19 effect on a new ambient particulate matter standard (PM₁₀). *Aerosol Sci. Technol.* 7: 467-473.
- 20 Lynch, A. J.; McQuaker, N. R.; Brown, D. F. (1980) ICP/AES analysis and the composition of airborne and soil
21 materials in the vicinity of a lead/zinc smelter complex. *J. Air Pollut. Control Assoc.* 30: 257-260.
- 22 Mader, B. T.; Flagan, R. C.; Seinfeld, J. H. (2001) Sampling atmospheric carbonaceous aerosols using a particle trap
23 impactor/denuder sampler. *Environ. Sci. Technol.* 35: 4857-4867.
- 24 Mahanama, K. R. R.; Gundel, L. A.; Daisey, J. M. (1994) Selective fluorescence detection of polycyclic aromatic
25 hydrocarbons in environmental tobacco smoke and other airborne particles. *Int. J. Environ. Anal. Chem.*
26 56: 289-309.
- 27 Mäkelä, J. M.; Aalto, P.; Jokinen, V.; Pohja, T.; Nissinen, A.; Palmroth, S.; Markkanen, T.; Seitsonen, K.;
28 Lihavainen, H.; Kulmala, M. (1997) Observations of ultrafine aerosol particle formation and growth in boreal
29 forest. *Geophys. Res. Lett.* 24: 1219-1222.
- 30 Malm, W. C.; Sisler, J. F.; Huffman, D.; Eldred, R. A.; Cahill, T. A. (1994) Spatial and seasonal trends in particle
31 concentration and optical extinction in the United States. *J. Geophys. Res. [Atmos.]* 99: 1347-1370.
- 32 Mamane, Y.; Willis, R.; Conner, T. (2001) Evaluation of computer-controlled scanning electron microscopy applied
33 to an ambient urban aerosol sample. *Aerosol Sci. Technol.* 34: 97-107.
- 34 Marple, V. A.; Chien, C. M. (1980) Virtual impactors: a theoretical study. *Environ. Sci. Technol.* 14: 976-985.
- 35 Marple, V. A.; Olson, B. A. (1995) A high volume PM₁₀/PM_{2.5}/PM_{1.0} trichotomous sampler. In: *Particulate matter:*
36 *health and regulatory issues: proceedings of an international specialty conference; April; Pittsburgh, PA.*
37 *Pittsburgh, PA: Air & Waste Management Association; pp. 237-261. (A&WMA publication VIP-49).*
- 38 Marple, V. A.; Liu, B. Y. H.; Burton, R. M. (1990) High-volume impactor for sampling fine and coarse particles. *J.*
39 *Air Waste Manage. Assoc.* 40: 762-767.
- 40 Marple, V. A.; Rubow, K. L.; Behm, S. M. (1991) A microorifice uniform deposit impactor (MOUDI): description,
41 calibration, and use. *Aerosol Sci. Technol.* 14: 434-446.
- 42 Masuda, H.; Nakasita, S. (1988) Classification performance of a rectangular jet virtual impactor-effects of nozzle
43 width ratio of collection nozzle to acceleration nozzle. *J. Aerosol Sci.* 19: 243-252.
- 44 Masuda, H.; Hochrainer, D.; Stöber, W. (1979) An improved virtual impactor for particle classification and
45 generation of test aerosols with narrow size distributions. *J. Aerosol Sci.* 10: 275-287.
- 46 McGovern, F. M. (1999) An analysis of condensation nuclei levels at Mace Head, Ireland. *Atmos. Environ.*
47 33: 1711-1723.
- 48 McGovern, F. M.; Jennings, S. G.; O'Connor, T. C.; Simmonds, P. G. (1996) Aerosol and trace gas measurements
49 during the Mace Head experiment. *Atmos. Environ.* 30: 3891-3902.
- 50 McInnes, L. M.; Quinn, P. K.; Covert, D. S.; Anderson, T. L. (1996) Gravimetric analysis, ionic composition, and
51 associated water mass of the marine aerosol. *Atmos. Environ.* 30: 869-884.
- 52 McMurry, P. H. (2000) A review of atmospheric aerosol measurements. *Atmos. Environ.* 34: 1959-1999.
- 53 McMurry, P. H.; Friedlander, S. K. (1979) New particle formation in the presence of an aerosol. *Atmos. Environ.*
54 13: 1635-1651.
- 55 McMurry, P. H.; Stolzenburg, M. R. (1989) On the sensitivity of particle size to relative humidity for Los Angeles
56 aerosols. *Atmos. Environ.* 23: 497-507.

- 1 McMurry, P. H.; Woo, K. S.; Weber, R.; Chen, D.-R.; Pui, D. Y. H. (2000) Size distributions of 3 to 10 nm
2 atmospheric particles: implications for nucleation mechanisms. *Philos. Trans. R. Soc. London Ser. A*
3 358: 2625-2642.
- 4 McQuaker, N. R.; Kluckner, P. D.; Chang, G. N. (1979) Calibration of an inductively coupled plasma-atomic
5 emission spectrometer for the analysis of environmental materials. *Anal. Chem.* 51: 888-895.
- 6 Meyer, A. S., Jr.; Boyd, C. M. (1959) Determination of water by titration with coulometrically generated Karl
7 Fischer reagent. *Anal. Chem.* 31: 215-219.
- 8 Meyer, M. B.; Rupprecht, E. G. (1996) Particulate matter sampling methods: the importance of standardization.
9 *J. Aerosol. Sci.* 27(suppl. 1): S349-S350.
- 10 Meyer, M. B.; Rupprecht, E.; Patashnick, H. (1995) Considerations for the sampling and measurement of ambient
11 particulate matter. In: *Particulate matter: health and regulatory issues: proceedings of an international*
12 *specialty conference; April; Pittsburgh, PA. Pittsburgh, PA: Air & Waste Management Association;*
13 *pp. 204-210. (A&WMA publication VIP-49).*
- 14 Meyer, M. B.; Patashnick, H.; Ambis, J. L.; Rupprecht, E. (2000) Development of a sample equilibration system for
15 the TEOM continuous PM monitor. *J. Air Waste Manage. Assoc.* 50: 1345-1349.
- 16 Middlebrook, A. M.; Murphy, D. M.; Thomson, D. S. (1998) Observations of organic material in individual marine
17 particles at Cape Grim during the first aerosol characterization experiment (ACE 1). *J. Geophys. Res.*
18 103: 16475-16483.
- 19 Middlebrook, A. M.; et al. (2002) A comparison of particle mass spectrometers during the 1999 Atlanta Supersites
20 project. *J. Geophys. Res.*: in press.
- 21 Mignacca, D.; Stubbs, K. (1999) Effects of equilibration temperature on PM₁₀ concentrations from the TEOM
22 method in the Lower Fraser Valley. *J. Air Waste Manage. Assoc.* 49: 1250-1254.
- 23 Miller, F. J.; Gardner, D. E.; Graham, J. A.; Lee, R. E., Jr.; Wilson, W. E.; Bachmann, J. D. (1979) Size
24 considerations for establishing a standard for inhalable particles. *J. Air Pollut. Control Assoc.* 29: 610-615.
- 25 Misra, C.; Geller, M. D.; Shah, P.; Sioutas, C.; Solomon, P. A. (2001) Development and evaluation of a continuous
26 coarse (PM₁₀-PM_{2.5}) particle monitor. *J. Air Waste Manage. Assoc.* 51: 1309-1317.
- 27 Modey, W. K.; Pang, Y.; Eatough, N. L.; Eatough, D. J. (2001) Fine particulate (PM_{2.5}) composition in Atlanta,
28 USA: assessment of the particle concentrator-Brigham Young University organic sampling system,
29 PC-BOSS, during the EPA supersite study. *Atmos. Environ.* 35: 6493-6502.
- 30 Moosmüller, H.; Arnott, W. P.; Rogers, C. F. (1998) Photoacoustic and filter measurements related to aerosol light
31 absorption during the Northern Front Range Air Quality Study (Colorado 1996-1997). *J. Geophys. Res.*
32 103: 28,149-28,157.
- 33 Morawska, L.; Bofinger, N. D.; Kocis, L.; Nwankwoala, A. (1998) Submicrometer and supermicrometer particles
34 from diesel vehicle emissions. *Environ. Sci. Technol.* 32: 2033-2042.
- 35 Mueller, P. K.; Collins, J. F. (1980) Development of a particulate sulfate analyzer. Palo Alto, CA: Electric Power
36 Research Institute; report no. P-1382F.
- 37 Mueller, P. K.; Fung, K. K.; Heisler, S. L.; Grosjean, D.; Hidy, G. M. (1982) Atmospheric particulate carbon
38 observations in urban and rural areas of the United States. In: Wolff, G. T.; Klimisch, R. L., eds. *Particulate*
39 *carbon: atmospheric life cycle: proceedings of an international symposium; October 1980; Warren, MI.*
40 *New York, NY: Plenum Press; pp. 343-370.*
- 41 Mueller, P. K.; Hansen, D. A.; Watson, J. G., Jr. (1986) The subregional cooperative electric utility, Department of
42 Defense, National Park Service, and EPA study (SCENES) on visibility: an overview. Palo Alto, CA: Electric
43 Power Research Institute; report no. EA-4664-SR.
- 44 Mukerjee, S.; Ellenson, W. D.; Lewis, R. G.; Stevens, R. K.; Somerville, M. C.; Shadwick, D. S.; Willis, R. D.
45 (1997) An environmental scoping study in the lower Rio Grande Valley of Texas-III. residential
46 microenvironmental monitoring for air, house dust, and soil. *Environ. Int.* 23: 657-673.
- 47 Munksgaard, N. C.; Parry, D. L. (1998) Lead isotope ratios determined by ICP-MS: monitoring of mining-derived
48 metal particulates in atmospheric fallout, Northern Territory, Australia. *Sci. Total Environ.* 217: 113-126.
- 49 Murphy, D. M.; Thomson, D. S. (1997) Chemical composition of single aerosol particles at Idaho Hill: negative ion
50 measurements. *J. Geophys. Res.* 102: 6353-6368.
- 51 Nadkarni, R. A. (1975) Multielement analysis of coal and coal fly ash standards by instrumental neutron activation
52 analysis. *Radiochem. Radioanal. Lett.* 21: 161-176.
- 53 Nam, S.-H.; Masamba, W. R. L.; Montaser, A. (1993) Investigation of helium inductively coupled plasma-mass
54 spectrometry for the detection of metals and nonmetals in aqueous solutions. *Anal. Chem.* 65: 2784-2790.
- 55 NARSTO. (2003) Fine particle assessment (review draft). Oak Ridge, TN: U.S. Department of Energy, Oak Ridge
56 National Laboratory, North American Research Strategy for Tropospheric Ozone, Quality Systems Science
57 Center. Available: <http://www.cgenv.com/Narsto/> (22 April 2003).

- 1 National Research Council. (1993) Protecting visibility in national parks and wilderness areas. Washington, DC:
2 National Academy Press. 3v.
- 3 Nelson, M. P.; Zugates, C. T.; Treado, P. J.; Casucio, G. S.; Exline, D. L.; Schlaegle, S. F. (2000) Combining Raman
4 chemical imaging scanning electron microscopy (SEM) to characterize ambient fine particulate. *Aerosol Sci.*
5 *Technol.* 34: 108-117.
- 6 Neubauer, K. R.; Johnston, M. V.; Wexler, A. S. (1998) Humidity effects on the mass spectra of single aerosol
7 particles. *Atmos. Environ.* 32: 2521-2529.
- 8 Nham, T. T. (1996) Cool plasma technique for the ultra-trace level determination of 56Fe, 40Ca, 39K, 7Li, 24Mg
9 and 23Na for semi-conductor applications. Mulgrave, Victoria, Australia: Varian Australia Pty Ltd; ICP-MS
10 instruments at work no. ICP-MS-7. Available:
11 <http://www.varianinc.com/cgi-bin/nav?varinc/docs/osi/icpms/atwork/icpms7&cid=680052> [18 January,
12 2002].
- 13 Noble, C. A.; Prather, K. A. (1996) Real-time measurement of correlated size and composition profiles of individual
14 atmospheric aerosol particles. *Environ. Sci. Technol.* 30: 2667-2680.
- 15 Noble, C. A.; Prather, K. A. (1998) Single particle characterization of albuterol metered dose inhaler aerosol in near
16 real-time. *Aerosol Sci. Technol.* 29: 294-306.
- 17 Noble, C. A.; Vanderpool, R. W.; Peters, T. M.; McElroy, F. F.; Gemmill, D. B.; Wiener, R. W. (2001) Federal
18 reference and equivalent methods for measuring fine particulate matter. *Aerosol Sci. Technol.* 34: 457-464.
- 19 Noël, M. A.; Topart, P. A. (1994) High-frequency impedance analysis of quartz crystal microbalances. 1. General
20 considerations. *Anal. Chem.* 66: 484-491.
- 21 Novakov, T.; Corrigan, C. E.; Penner, J. E.; Chuang, C. C.; Rosario, O.; Mayol Bracero, O. L. (1997) Organic
22 aerosols in the Caribbean trade winds: a natural source? *J. Geophys. Res.* 102: 21307-21313.
- 23 O'Dowd, C. D.; Aalto, P.; Hämeri, K.; Kulmala, M.; Hoffmann, T. (2002) Atmospheric particles from organic
24 vapours. *Nature (London, U. K.)* 416: 497-498.
- 25 Obeidi, F. D.; Eatough, D. J. (2002) Continuous measurement of semi-volatile fine particulate mass in Provo, UT.
26 *Aerosol Sci. Technol.* 36: 191-203.
- 27 Obeidi, F.; Eatough, N. L.; Eatough, D. J. (2002) Use of the RAMS to measure semivolatile fine particulate matter at
28 Riverside and Bakersfield, California. *Aerosol Sci. Technol.* 36: 204-216.
- 29 Odum, J. R.; Yu, J.; Kamens, R. M. (1994) Modeling the mass transfer of semivolatile organics in combustion
30 aerosols. *Environ. Sci. Technol.* 28: 2278-2285.
- 31 Ohta, S.; Okita, T. (1990) A chemical characterization of atmospheric aerosol in Sapporo. *Atmos. Environ. Part A*
32 24A: 815-822.
- 33 Ohta, S.; Hori, M.; Yamagata, S.; Murao, N. (1998) Chemical characterization of atmospheric fine particles in
34 Sapporo with determination of water content. *Atmos. Environ.* 32: 1021-1025.
- 35 Olin, J. G.; Sem, G. J. (1971) Piezoelectric microbalance for monitoring the mass concentration of suspended
36 particles. *Atmos. Environ.* 5: 653-668.
- 37 Olmez, I. (1989) Trace element signatures in groundwater pollution. In: Watson, J. G., ed. Receptor models in air
38 resources management: an international specialty conference; February 1988; San Francisco, CA. Pittsburgh,
39 PA: Air & Waste Management Association; pp. 3-11. (APCA transactions series: no. 14).
- 40 Ondov, J. M. (1996) Particulate tracers for source attribution: potential for application to California's San Joaquin
41 Valley. *J. Aerosol Sci.* 27(suppl. 1): S687-S688.
- 42 Ondov, J. M.; Kelly, W. R.; Holland, J. Z.; Lin, Z. C.; Wight, S. A. (1992) Tracing fly ash emitted from a coal-fired
43 power plant with enriched rare-earth isotopes: an urban scale test. *Atmos. Environ. Part B* 26B: 453-462.
- 44 Ondov, J. M.; Divita, F., Jr. (1993) Size spectra for trace elements in urban aerosol particles by instrumental neutron
45 activation analysis. *J. Radioanal. Nucl. Chem.* 167: 247-258.
- 46 Ono, D. M.; Hardebeck, E.; Parker, J.; Cox, B. G. (2000) Systematic biases in measured PM₁₀ values with U.S.
47 Environmental Protection Agency-approved samplers at Owens Lake, California. *J. Air Waste Manage.*
48 *Assoc.* 50: 1144-1156.
- 49 Pak, S. S.; Liu, B. Y. H.; Rubow, K. L. (1992) Effect of coating thickness on particle bounce in inertial impactors.
50 *Aerosol Sci. Technol.* 16: 141-150.
- 51 Pang, Y.; Ren, Y.; Obeidi, F.; Hastings, R.; Eatough, D. J.; Wilson, W. E. (2001) Semi-volatile species in PM_{2.5}:
52 comparison of integrated and continuous samplers for PM_{2.5} research or monitoring. *J. Air Waste Manage.*
53 *Assoc.* 51: 25-36.
- 54 Pang, Y.; Eatough, N. L.; Wilson, J.; Eatough, D. J. (2002a) Effect of semivolatile material on PM_{2.5} measurement
55 by the PM_{2.5} federal reference method sampler at Bakersfield, California. *Aerosol Sci. Technol.* 36: 289-299.
- 56 Pang, Y.; Eatough, N. L.; Eatough, D. J. (2002b) PM_{2.5} semivolatile organic material at Riverside, CA: implications
57 for the PM_{2.5} federal reference method sampler. *Aerosol Sci. Technol.* 36: 277-288.

- 1 Pankow, J. F. (1987) Review and comparative analysis of the theories on partitioning between the gas and aerosol
2 particulate phases in the atmosphere. *Atmos. Environ.* 21: 2275-2283.
- 3 Pankow, J. F. (1994a) An absorption model of the gas/aerosol partitioning involved in the formation of secondary
4 organic aerosol. *Atmos. Environ.* 28: 189-193.
- 5 Pankow, J. F. (1994b) An absorption model of gas/particle partitioning of organic compounds in the atmosphere.
6 *Atmos. Environ.* 28: 185-188.
- 7 Pankow, J. F.; Bidleman, T. F. (1991) Effects of temperature, *TSP* and per cent non-exchangeable material in
8 determining the gas-particle partitioning of organic compounds. *Atmos. Environ. Part A* 25: 2241-2249.
- 9 Pankow, J. F.; Storey, J. M. E.; Yamasaki, H. (1993) Effects of relative humidity on gas/particle partitioning of
10 semivolatile organic compounds to urban particulate matter. *Environ. Sci. Technol.* 27: 2220-2226.
- 11 Parmar, S. S.; Grosjean, D. (1990) Laboratory tests of KI and alkaline annular denuders. *Atmos. Environ. Part A*
12 24: 2695-2698.
- 13 Patashnick, H.; Rupprecht, G.; Ambs, J. L.; Meyer, M. B. (2001) Development of a reference standard for
14 particulate matter mass in ambient air. *Aerosol Sci. Technol.* 34: 42-45.
- 15 Pellizzari, E. D.; Krost, K. J. (1984) Chemical transformations during ambient air sampling for organic vapors. *Anal.*
16 *Chem.* 56: 1813-1819.
- 17 Peng, C.; Chan, C. K. (2001) The water cycles of water-soluble organic salts of atmospheric importance.
18 *Atmos. Environ.* 35: 1183-1192.
- 19 Penner, J. E.; Novakov, T. (1996) Carbonaceous particles in the atmosphere: a historical perspective to the fifth
20 international conference on carbonaceous particles in the atmosphere. *J. Geophys. Res. [Atmos.]*
21 101: 19,373-19,378.
- 22 Perry, K. D.; Hobbs, P. V. (1994) Further evidence for particle nucleation in clear air adjacent to marine cumulus
23 clouds. *J. Geophys. Res. [Atmos.]* 99: 22,803-22,818.
- 24 Perry, K. D.; Cahill, T. A.; Schnell, R. C.; Harris, J. M. (1999) Long-range transport of anthropogenic aerosols to the
25 National Oceanic and Atmospheric Administration baseline station at Mauna Loa Observatory, Hawaii.
26 *J. Geophys. Res. Atmos.* 104: 18,521-18,533.
- 27 Peters, A.; Liu, E.; Verrier, R. L.; Schwartz, J.; Gold, D. R.; Mittleman, M.; Baliff, J.; Oh, J. A.; Allen, G.;
28 Monahan, K.; Dockery, D. W. (2000) Air pollution and incidence of cardiac arrhythmia. *Epidemiology*
29 11: 11-17.
- 30 Peters, T. M.; Vanderpool, R. W.; Wiener, R. W. (2001a) Design and calibration of the EPA PM_{2.5} well impactor
31 ninety-six (WINS). *Aerosol Sci. Technol.* 34: 389-397.
- 32 Peters, T. M.; Norris, G. A.; Vanderpool, R. W.; Gemmill, D. B.; Wiener, R. W.; Murdoch, R. W.; McElroy, F. F.;
33 Pitchford, M. (2001b) Field performance of PM_{2.5} federal reference method samplers. *Aerosol Sci. Technol.*
34 34: 433-443.
- 35 Peters, T. M.; Gussman, R. A.; Kenny, L. C.; Vanderpool, R. W. (2001c) Evaluation of PM_{2.5} size selectors used in
36 speciation samplers. *Aerosol Sci. Technol.* 34: 422-429.
- 37 Petzold, A.; Niessner, R. (1996) Photoacoustic soot sensor for in-situ black carbon monitoring. *Appl. Phys. B:*
38 *Lasers Opt.* 63: 191-197.
- 39 Petzold, A.; Kopp, C.; Niessner, R. (1997) The dependence of the specific attenuation cross-section on black carbon
40 mass fraction and particle size. *Atmos. Environ.* 31: 661-672.
- 41 Pilinis, C.; Seinfeld, J. H.; Grosjean, D. (1989) Water content of atmospheric aerosols. *Atmos. Environ.*
42 23: 1601-1606.
- 43 Piorek, S. (1994) Modern, PC based, high resolution portable EDXRF analyzer offers laboratory performance for
44 field, in-situ analysis of environmental contaminants. *Nucl. Instr. Meth. Phys. Res. A* 353: 528-533.
- 45 Pirrone, N.; Keeler, G. J. (1996) The Rouge River watershed pollution by trace elements: atmospheric depositions
46 and emission sources. *Water Sci. Technol.* 33: 267-275.
- 47 Plantz, M. (1996) Common molecular ion interferences in ICP-MS. Mulgrave, Victoria, Australia: Varian Australia
48 Pty Ltd; ICP-MS instruments at work no. ICP-MS-6. Available:
49 <http://www.varianinc.com/cgi-bin/nav?varinc/docs/osi/icpms/atwork/index&cid=680052> [18 January, 2002].
- 50 Poor, N.; Clark, T.; Nye, L.; Tamanini, T.; Tate, K.; Stevens, R.; Atkeson, T. (2002) Field performance of
51 dichotomous sequential PM air samplers. *Atmos. Environ.* 36: 3289-3298.
- 52 Pope, C. A., III; Thun, M. J.; Namboodiri, M. M.; Dockery, D. W.; Evans, J. S.; Speizer, F. E.; Heath, C. W., Jr.
53 (1995) Particulate air pollution as a predictor of mortality in a prospective study of U.S. adults. *Am. J. Respir.*
54 *Crit. Care Med.* 151: 669-674.
- 55 Potts, P. J.; Webb, P. C. (1992) X-ray fluorescence spectrometry. *J. Geochem. Explor.* 44: 251-296.
- 56 Radke, L. F.; Hobbs, P. V. (1991) Humidity and particle fields around some small cumulus clouds. *J. Atmos. Sci.*
57 48: 1190-1193.

- 1 Raes, F.; Van Dingenen, R.; Cuevas, E.; Van Velthoven, P. F. J.; Prospero, J. M. (1997) Observations of aerosols in
2 the free troposphere and marine boundary layer of the subtropical Northeast Atlantic: discussion of processes
3 determining their size distribution. *J. Geophys. Res. [Atmos.]* 102: 21315-21328.
- 4 Ranweiler, L. E.; Moyers, J. L. (1974) Atomic absorption procedure for analysis of metals in atmospheric particulate
5 matter. *Environ. Sci. Technol.* 8: 152-156.
- 6 Rao, A. K.; Whitby, K. T. (1977) Nonideal collection characteristics of single stage and cascade impactors. *Am. Ind.*
7 *Hyg. Assoc. J.* 38: 174-177.
- 8 Rao, A. K.; Whitby, K. T. (1978) Non-ideal collection characteristics of inertial impactors--I. single-stage impactors
9 and solid particles. *J. Aerosol Sci.* 9: 77-86.
- 10 Ravenhall, D. G.; Forney, L. J.; Jazayeri, M. (1978) Aerosol sizing with a slotted virtual impactor. *J. Colloid*
11 *Interface Sci.* 65: 108-117.
- 12 Reid, J. S.; Cahill, T. A.; Wakabayashi, P. H.; Dunlap, M. R. (1994) Geometric/aerodynamic equivalent diameter
13 ratios of ash aggregate aerosols collected in burning Kuwaiti well fields. *Atmos. Environ.* 28: 2227-2234.
- 14 Reilly, P. T. A.; Gieray, R. A.; Whitten, W. B.; Ramsey, J. M. (1998) Real-time characterization of the organic
15 composition and size of individual diesel engine smoke particles. *Environ. Sci. Technol.* 32: 2672-2679.
- 16 Reist, P. C. (1984) Introduction to aerosol science. New York, NY: Macmillan Publishing Company.
- 17 Reist, P. C. (1993) Introduction to aerosol science. New York, NY: McGraw-Hill.
- 18 Risse, U.; Flammenkamp, E.; Kettrup, A. (1996) Determination of aromatic hydrocarbons in air using diffusion
19 denuders. *Fresenius' J. Anal. Chem.* 356: 390-395.
- 20 Roberts, R. A.; Corkill, J. (1998) Grass seed field smoke and its impact on respiratory health. *J. Environ. Health* 60
21 (June): 10-16.
- 22 Rounds, S. A.; Pankow, J. F. (1990) Application of a radial diffusion model to describe gas/particle sorption
23 kinetics. *Environ. Sci. Technol.* 24: 1378-1386.
- 24 Rounds, S. A.; Tiffany, B. A.; Pankow, J. F. (1993) Description of gas/particle sorption kinetics with an intraparticle
25 diffusion model: desorption experiments. *Environ. Sci. Technol.* 27: 366-377.
- 26 Rumburg, B.; Alldredge, R.; Claiborn, C. (2001) Statistical distributions of particulate matter and the error
27 associated with sampling frequency. *Atmos. Environ.* 35: 2907-2920.
- 28 Rupprecht, G.; Patashnick, H.; Beeson, D. E.; Green, R. N.; Meyer, M. B. (1995) A new automated monitor for the
29 measurement of particulate carbon in the atmosphere. In: *Particulate matter: health and regulatory issues:*
30 *proceedings of an international specialty conference; April; Pittsburgh, PA. Pittsburgh, PA: Air & Waste*
31 *Management Association; pp. 309-319. (A&WMA publication VIP-49).*
- 32 Sakata, K.; Kawabata, K. (1994) Reduction of fundamental polyatomic ions in inductively coupled plasma mass
33 spectrometry. *Spectrochim. Acta* 49B: 1027-1038.
- 34 Saxena, P.; Hildemann, L. M. (1996) Water-soluble organics in atmospheric particles: a critical review of the
35 literature and applications of thermodynamics to identify candidate compounds. *J. Atmos. Chem.* 24: 57-109.
- 36 Saxena, P.; Hildemann, L. M.; McMurry, P. H.; Seinfeld, J. H. (1995) Organics alter hygroscopic behavior of
37 atmospheric particles. *J. Geophys. Res. [Atmos.]* 100: 18,755-18,770.
- 38 Schmid, H.; Laskus, L.; Abraham, J. H.; Baltensperger, U.; Lavanchy, V.; Bizjak, M.; Burba, P.; Cachier, H.; Crow,
39 D.; Chow, J.; Gnauk, T.; Even, A.; Ten Brink, H. M.; Giesen, K.-P.; Hitznerberger, R.; Hueglin, C.;
40 Maenhaut, W.; Pio, C.; Carvalho, A.; Putaud, J.-P.; Toom-Sauntry, D.; Puxbaum, H. (2001) Results of the
41 "carbon conference" international aerosol carbon round robin test stage I. *Atmos. Environ.* 35: 2111-2121.
- 42 Schröder, F.; Ström, J. (1997) Aircraft measurements of submicrometer aerosol particles (> 7 nm) in the midaltitude
43 free troposphere and tropopause region. *Atmos. Res.* 44: 333-356.
- 44 Schwartz, J.; Dockery, D. W.; Neas, L. M. (1996) Is daily mortality associated specifically with fine particles? *J. Air*
45 *Waste Manage. Assoc.* 46: 927-939.
- 46 Seinfeld, J. H.; Pandis, S. N. (1998) Atmospheric chemistry and physics: from air pollution to climate change.
47 New York, NY: John Wiley & Sons, Inc.
- 48 Sem, G. J.; Tsurubayashi, K.; Homma, K. (1977) Performance of the piezoelectric microbalance respirable aerosol
49 sensor. *Am. Ind. Hyg. Assoc. J.* 38: 580-588.
- 50 Shah, J. J.; Rau, J. A. (1990) Carbonaceous methods comparison study: interlaboratory round robin interpretation
51 results. Sacramento, CA: California Air Resources Board. Available:
52 <http://www.arb.ca.gov/research/apr/past/pm.htm> (21 March 2002).
- 53 Silva, P. J.; Prather, K. A. (1997) On-line characterization of individual particles from automobile emissions.
54 *Environ. Sci. Technol.* 31: 3074-3080.
- 55 Simon, P. K.; Dasgupta, P. K. (1995) Continuous automated measurement of the soluble fraction of atmospheric
56 particulate matter. *Anal. Chem.* 67: 71-78.

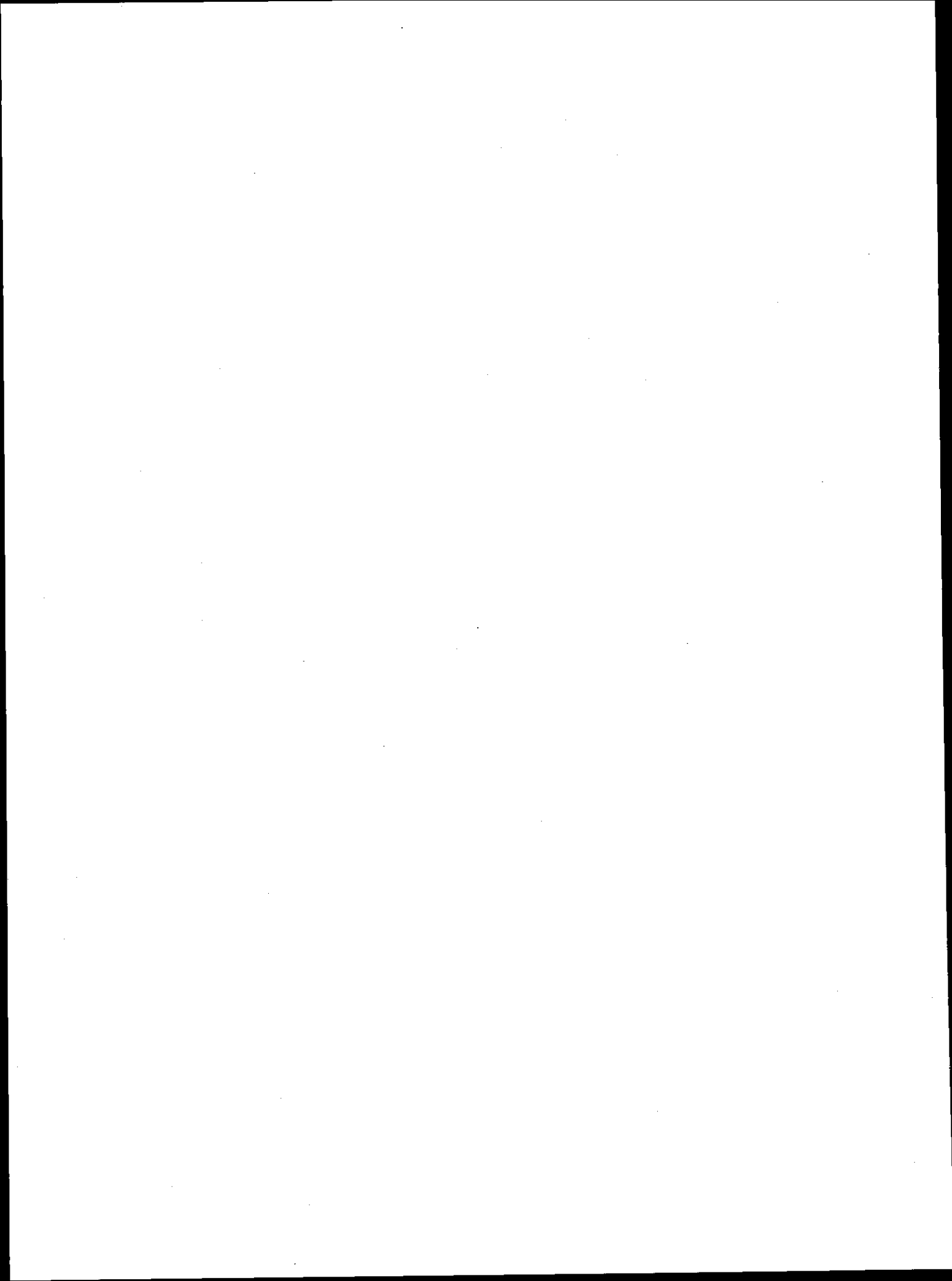
- 1 Sioutas, C.; Koutrakis, P. (1996) Inertial separation of ultrafine particles using a condensational growth/virtual
2 impaction system. *Aerosol Sci. Technol.* 25: 424-436.
- 3 Sioutas, C.; Koutrakis, P.; Burton, R. M. (1994a) Development of a low cutpoint slit virtual impactor for sampling
4 ambient fine particles. *J. Aerosol Sci.* 25: 1321-1330.
- 5 Sioutas, C.; Koutrakis, P.; Burton, R. M. (1994b) A high-volume small cutpoint virtual impactor for separation of
6 atmospheric particulate from gaseous pollutants. *Part. Sci. Technol.* 12: 207-221.
- 7 Sioutas, C.; Koutrakis, P.; Olson, B. A. (1994c) Development and evaluation of a low cutpoint virtual impactor.
8 *Aerosol Sci. Technol.* 21: 223-235.
- 9 Sioutas, C.; Koutrakis, P.; Wolfson, J. M. (1994d) Particle losses in glass honeycomb denuder samplers. *Aerosol*
10 *Sci. Technol.* 21: 137-148.
- 11 Sioutas, C.; Koutrakis, P.; Burton, R. M. (1995a) A technique to expose animals to concentrated fine ambient
12 aerosols. *Environ. Health Perspect.* 103: 172-177.
- 13 Sioutas, D.; Koutrakis, P.; Ferguson, S. T.; Burton, R. M. (1995b) Development and evaluation of a prototype
14 ambient particle concentrator for inhalation exposure studies. *Inhalation Toxicol.* 7: 633-644.
- 15 Sioutas, C.; Koutrakis, P.; Wolfson, J. M.; Azaroff, L. S.; Mulik, J. D. (1996a) Field evaluation of a glass
16 honeycomb denuder/filter pack system to collect atmospheric gases and particles. In: Gay, B. W.; Fuerst,
17 R. G.; Jayanty, R. K. M., eds. *Measurement of toxic and related air pollutants: proceedings of a conference;*
18 *May, 1994; Durham, NC. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of*
19 *Research and Development; report no. EPA/600/R-94/136; pp. 426-435.*
- 20 Sioutas, C.; Wang, P. Y.; Ferguson, S. T.; Koutrakis, P.; Mulik, J. D. (1996b) Laboratory and field evaluation of an
21 improved glass honeycomb denuder/filter pack sampler. *Atmos. Environ.* 30: 885-895.
- 22 Sioutas, C.; Koutrakis, P.; Wang, P.-Y.; Babich, P.; Wolfson, J. M. (1999) Experimental investigation of pressure
23 drop with particle loading in Nuclepore filters. *Aerosol Sci. Technol.* 30: 71-83.
- 24 Sioutas, C.; Kim, S.; Chang, M.; Terrell, L. L.; Gong, H., Jr. (2000) Field evaluation of a modified DataRAM MIE
25 scattering monitor for real-time PM_{2.5} mass concentration measurements. *Atmos. Environ.* 34: 4829-4838.
- 26 Smith, K. R.; Kim, S.; Recendez, J. J.; Sioutas, C.; Pinkerton, K. E. (2003) Airborne particles of the California
27 Central Valley alter the lungs of health adult rats. *Environ. Health Perspect.*
- 28 Solomon, P. A.; Moyers, J. L.; Fletcher, R. A. (1983) High-volume dichotomous virtual impactor for the
29 fractionation and collection of particles according to aerodynamic size. *Aerosol Sci. Technol.* 2: 455-464.
- 30 Solomon, P. A.; Salmon, L. G.; Fall, T.; Cass, G. R. (1992) Spatial and temporal distribution of atmospheric nitric
31 acid and particulate nitrate concentrations in the Los Angeles area. *Environ. Sci. Technol.* 26: 1596-1601.
- 32 Song, X.-H.; Faber, N. M.; Hopke, P. K.; Suess, D. T.; Prather, K. A.; Schauer, J. J.; Cass, G. R. (2001) Source
33 apportionment of gasoline and diesel by multivariate calibration based on single particle mass spectral data.
34 *Anal. Chim. Acta* 446: 329-343.
- 35 Speer, R. E.; Barnes, H. M.; Brown, R. (1997) An instrument for measuring the liquid water content of aerosols.
36 *Aerosol Sci. Technol.* 27: 50-61.
- 37 Spengler, J. D.; Thurston, G. D. (1983) Mass and elemental composition of fine and coarse particles in six U.S.
38 cities. *J. Air Pollut. Control Assoc.* 33: 1162-1171.
- 39 Stahlschmidt, T.; Schulz, M.; Dannecker, W. (1997) Application of total-reflection X-ray fluorescence for the
40 determination of lead, calcium and zinc in size-fractionated marine aerosols. *Spectrochim. Acta B*
41 52: 995-1001.
- 42 Stein, S. W.; Turpin, B. J.; Cai, X.; Huang, P.-F.; McMurry, P. H. (1994) Measurements of relative
43 humidity-dependent bounce and density for atmospheric particles using the DMA-impactor technique. *Atmos.*
44 *Environ.* 28: 1739-1746.
- 45 Stevens, R. K.; O'Keefe, A. E.; Ortman, G. C. (1969) Absolute calibration of a flame photometric detector to
46 volatile sulfur compounds at sub-part-per-million levels. *Environ. Sci. Technol.* 3: 652-655.
- 47 Stevens, R. K.; Mulik, J. D.; O'Keefe, A. E.; Krost, K. J. (1971) Gas chromatography of reactive sulfur gases in air
48 at the parts-per-billion level. *Anal. Chem.* 43: 827-831.
- 49 Stolzenburg, M. R.; Hering, S. V. (2000) Method for the automated measurement of fine particle nitrate in the
50 atmosphere. *Environ. Sci. Technol.* 34: 907-914.
- 51 Streit, N.; Weingartner, E.; Zellweger, C.; Schwikowski, M.; Gäggeler, H. W.; Baltensperger, U. (2000)
52 Characterization of size-fractionated aerosol from the Jungfraujoch (3580 m asl) using total reflection x-ray
53 fluorescence (TXRF). *Int. J. Environ. Anal. Chem.* 76: 1-16.
- 54 Strobel, H. A.; Heineman, W. R. (1989) *Chemical instrumentation: a systematic approach.* 3rd ed. New York, NY:
55 Wiley and Sons, Inc.

- 1 Strommen, M. R.; Kamens, R. M. (1997) Development and application of a dual-impedance radial diffusion model
2 to simulate the partitioning of semivolatile organic compounds in combustion aerosols. *Environ. Sci. Technol.*
3 31: 2983-2990.
- 4 Strothmann, J. A.; Schiermeier, F. A. (1979) Documentation of the regional air pollution study (RAPS) and related
5 investigations in the St. Louis air quality control region. Research Triangle Park, NC: U.S. Environmental
6 Protection Agency, Environmental Science Research Laboratory; report no. EPA-600/4-79-076.
- 7 Suarez, A. E.; Caffrey, P. F.; Ondov, J. M.; Thauang, K. C. (1996) Size distribution of Ir-tagged soot from diesel
8 sanitation trucks. *J. Aerosol Sci.* 27(suppl. 1): S697-S698.
- 9 Suggs, J. C.; Burton, R. M. (1983) Spatial characteristics of inhalable particles in the Philadelphia metropolitan area.
10 *J. Air Pollut. Control Assoc.* 33: 688-691.
- 11 Suh, H. H.; Spengler, J. D.; Koutrakis, P. (1992) Personal exposures to acid aerosols and ammonia. *Environ. Sci.*
12 *Technol.* 26: 2507-2517.
- 13 Suh, H. H.; Koutrakis, P.; Spengler, J. D. (1994) The relationship between airborne acidity and ammonia in indoor
14 environments. *J. Exposure Anal. Environ. Epidemiol.* 4: 1-23.
- 15 Sutherland, J. L.; Bhardwaja, P. S. (1987) Composition of the aerosol in northern Arizona and southern Utah. In:
16 Bhardwaja, P. S., ed. *Transactions, Visibility Protection: Research and Policy Aspects*. Pittsburgh, PA: Air
17 Pollution Control Association; pp. 373-385.
- 18 Tan, S. H.; Horlick, G. (1986) Background spectral features in inductively coupled plasma/mass spectrometry. *Appl.*
19 *Spectrosc.* 40: 445-460.
- 20 Tang, I. N. (1980) Deliquescence properties and particle size change of hygroscopic aerosols. In: Willeke, K., ed.
21 *Generation of aerosols and facilities for exposure experiments*. Ann Arbor, MI: Ann Arbor Science
22 Publishers, Inc.; pp. 153-167.
- 23 Tang, H.; Lewis, E. A.; Eatough, D. J.; Burton, R. M.; Farber, R. J. (1994) Determination of the particle size
24 distribution and chemical composition of semi-volatile organic compounds in atmospheric fine particles with
25 a diffusion denuder sampling system. *Atmos. Environ.* 28: 939-947.
- 26 Tanner, R. L.; D'Ottavio, T.; Garber, R.; Newman, L. (1980) Determination of ambient aerosol sulfur using a
27 continuous flame photometric detection system. I. Sampling system for aerosol sulfate and sulfuric acid.
28 *Atmos. Environ.* 14: 121-127.
- 29 Thomson, D. S.; Murphy, D. M. (1994) Analyzing single aerosol particles in real time. *CHEMTECH* 24: 30-35.
- 30 Tobias, H. J.; Beving, D. E.; Ziemann, P. J.; Sakurai, H.; Zuk, M.; McMurry, P. H.; Zarling, D.; Wayrulonis, R.;
31 Kittelson, D. B. (2001) Chemical analysis of diesel engine nanoparticles using a nano-DMA/thermal
32 desorption particle beam mass spectrometer. *Environ. Sci. Technol.* 35: 2233-2243.
- 33 Tolocka, M. P.; Peters, T. M.; Vanderpool, R. W.; Chen, F. L.; Wiener, R. W. (2001a) On the modification of the
34 low flow-rate PM₁₀ dichotomous sampler inlet. *Aerosol Sci. Technol.* 34: 407-415.
- 35 Tolocka, M. P.; Solomon, P. A.; Mitchell, W.; Norris, G. A.; Gemmill, D. B.; Wiener, R. W.; Vanderpool, R. W.;
36 Homolya, J. B.; Rice, J. (2001b) East vs. west in the US: chemical characteristics of PM_{2.5} during the winter
37 of 1999. *Aerosol Sci. Technol.* 34: 88-96.
- 38 Török, S. B.; Lábár, J.; Schmeling, M.; Van Grieken, R. E. (1998) X-ray spectrometry. *Anal. Chem.* 70: 495R-517R.
- 39 Tsai, C.-J.; Cheng, Y.-H. (1996) Comparison of two ambient beta gauge PM₁₀ samplers. *J. Air Waste Manage.*
40 *Assoc.* 46: 142-147.
- 41 Tsai, C.-J.; Huang, H.-Y. (1995) Atmospheric aerosol sampling by an annular denuder system and a high-volume
42 PM₁₀ sampler. *Environ. Int.* 21: 283-291.
- 43 Turner, D. B. (1994) *Workbook of atmospheric dispersion estimates: an introduction to dispersion modeling*. 2nd ed.
44 Boca Raton, FL: Lewis Publishers.
- 45 Turner, J. R.; Hering, S. V. (1987) Greased and oiled substrates as bounce-free impaction surfaces. *J. Aerosol Sci.*
46 18: 215-224.
- 47 Turpin, B. J.; Huntzicker, J. J. (1991) Secondary formation of organic aerosol in the Los Angeles basin: a descriptive
48 analysis of organic and elemental carbon concentrations. *Atmos. Environ.* Part A 25: 207-215.
- 49 Turpin, B. J.; Huntzicker, J. J. (1995) Identification of secondary organic aerosol episodes and quantitation of
50 primary and secondary organic aerosol concentrations during SCAQS. *Atmos. Environ.* 29: 3527-3544.
- 51 Turpin, B. J.; Cary, R. A.; Huntzicker, J. J. (1990) An in situ, time-resolved analyzer for aerosol organic and
52 elemental carbon. *Aerosol Sci. Technol.* 12: 161-171.
- 53 Turpin, B. J.; Liu, S.-P.; Podolske, K. S.; Gomes, M. S. P.; Eisenreich, S. J.; McMurry, P. H. (1993) Design and
54 evaluation of a novel diffusion separator for measuring gas/particle distributions of semivolatile organic
55 compounds. *Environ. Sci. Technol.* 27: 2441-2449.
- 56 Turpin, B. J.; Huntzicker, J. J.; Hering, S. V. (1994) Investigation of organic aerosol sampling artifacts in the
57 Los Angeles basin. *Atmos. Environ.* 28: 3061-3071.

- 1 Turpin, B. J.; Saxena, P.; Andrews, E. (2000) Measuring and simulating particulate organics in the atmosphere:
2 problems and prospects. *Atmos. Environ.* 34: 2983-3013.
- 3 Tyler, G. (1992) ICP vs. AA: how do you choose? *Environ. Lab.* (October/November): 31-34.
- 4 U.S. Court of Appeals for the District of Columbia. (1999) *American Trucking Associations, Inc. vs. U.S.*
5 *Environmental Protection Agency*. 175 F.3d 1027 (D.C. Cir. 1999).
- 6 U.S. Environmental Protection Agency. (1982) Air quality criteria for particulate matter and sulfur oxides. Research
7 Triangle Park, NC: Office of Health and Environmental Assessment, Environmental Criteria and Assessment
8 Office; EPA report no. EPA-600/8-82-029aF-cF. 3v. Available from: NTIS, Springfield, VA; PB84-156777.
- 9 U.S. Environmental Protection Agency. (1996a) Air quality criteria for particulate matter. Research Triangle Park,
10 NC: National Center for Environmental Assessment-RTP Office; report nos. EPA/600/P-95/001aF-cF. 3v.
- 11 U.S. Environmental Protection Agency. (1996b) Review of the national ambient air quality standards for particulate
12 matter: policy assessment of scientific and technical information. OAQPS staff paper. Research Triangle
13 Park, NC: Office of Air Quality Planning and Standards; report no. EPA/452/R-96-013. Available from:
14 NTIS, Springfield, VA; PB97-115406REB.
- 15 U.S. Environmental Protection Agency. (1998) Monitoring PM_{2.5} in ambient air using designated reference of class I
16 equivalent methods. In: *Quality Assurance Handbook for Air Pollution Measurement Systems, V. II, Part II,*
17 *Section 2.12.* Research Triangle Park, NC: Research and Development, Environmental Monitoring Systems
18 Laboratory.
- 19 U.S. Environmental Protection Agency. (1999) Particulate matter (PM_{2.5}) speciation guidance. Final draft. Edition 1.
20 Research Triangle Park, NC: Office of Air Quality Planning and Standards. Available:
21 www.epa.gov/ttn/amtic/files/ambient/pm25/spec/specfinl.pdf [2000, October 11].
- 22 U.S. Environmental Protection Agency. (2001) List of designated reference and equivalent methods. Available:
23 <http://www.epa.gov/ttn/amtic/files/ambient/criteria/repmlist.pdf> [05 March 02].
- 24 U.S. Environmental Protection Agency. (2002a) Ambient monitoring technology information center (AMTIC).
25 Washington, DC: Office of Air Quality Planning and Standards; Monitoring and Quality Assurance Group.
26 Available: <http://www.epa.gov/ttn/amtic/> (20 March 2002).
- 27 U.S. Environmental Protection Agency. (2002b) Support center for regulatory air models. Washington, DC: Office
28 of Air Quality Planning and Standards. Available: <http://www.epa.gov/scram001> (21 March 2002).
- 29 Van Dingenen, R.; Raes, F.; Jensen, N. R. (1995) Evidence for anthropogenic impact on number concentration and
30 sulfate content of cloud-processed aerosol particles over the North Atlantic. *J. Geophys. Res.*
31 100: 21,057-21,067.
- 32 Van Loy, M.; Bahadori, T.; Wyzga, R.; Hartsell, B.; Edgerton, E. (2000) The Aerosol Research and Inhalation
33 Epidemiology Study (ARIES): PM_{2.5} mass and aerosol component concentrations and sampler
34 intercomparisons. *J. Air Waste Manage. Assoc.* 50: 1446-1458.
- 35 Vanderpool, R. W.; Peters, T. M.; Natarajan, S.; Gemmill, D. B.; Wiener, R. W. (2001) Evaluation of the loading
36 characteristics of the EPA WINS PM_{2.5} separator. *Aerosol Sci. Technol.* 34: 444-456.
- 37 Vasiliou, J. G.; Sorenson, D.; McMurry, P. H. (1999) Sampling at controlled relative humidity with a cascade
38 impactor. *Atmos. Environ.* 30: 1049-1056.
- 39 Venkataraman, C.; Lyons, J. M.; Friedlander, S. K. (1994) Size distributions of polycyclic aromatic hydrocarbons
40 and elemental carbon. 1. Sampling, measurement methods, and source characterization. *Environ. Sci.*
41 *Technol.* 28: 555-562.
- 42 Vincent, J. H. (1989) *Aerosol sampling: science and practice*. New York, NY: John Wiley & Sons.
- 43 Vincent, J. H. (1995) *Aerosol science for industrial hygienists*. Oxford, United Kingdom: Pergamon.
- 44 Wallace, J. C.; Hites, R. A. (1995) Computer-controlled low-volume air sampler for the measurement of semivolatile
45 organic compounds. *Environ. Sci. Technol.* 29: 2099-2106.
- 46 Wallace, L.; Howard-Reed, C. (2002) Continuous monitoring of ultrafine, fine, and coarse particles in a residence
47 for 18 months in 1999-2000. *J. Air Waste Manage. Assoc.* 52: 828-844.
- 48 Wang, H.-C.; John, W. (1987) Comparative bounce properties of particle materials. *Aerosol Sci. Technol.*
49 7: 285-299.
- 50 Wang, H.-C.; John, W. (1988) Characteristics of the Berner impactor for sampling inorganic ions. *Aerosol Sci.*
51 *Technol.* 8: 157-172.
- 52 Wang, P. Y. (1997) *Continuous aerosol mass measurement by flow obstruction*. Boston, MA: Harvard University,
53 School of Public Health.
- 54 Ward, M. D.; Buttry, D. A. (1990) In situ interfacial mass detection with piezoelectric transducers. *Science*
55 (Washington, DC) 249: 1000-1007.

- 1 Watson, J. G.; Chow, J. C.; Richards, L. W.; Neff, W. D.; Andersen, S. R.; Dietrich, D. L.; Houck, J. E.; Olmez, I.
2 (1988a) The 1987-88 metro Denver brown cloud study volume II: measurements. Reno, NV: Desert Research
3 Institute; final report no. 8810.1F2 (2 of 3).
- 4 Watson, J. G.; Chow, J. C.; Richards, L. W.; Neff, W. D.; Andersen, S. R.; Dietrich, D. L.; Houck, J. E.; Olmez, I.
5 (1988b) The 1987-88 metro Denver brown cloud study volume III: data interpretation. Reno, NV: Desert
6 Research Institute; final report no. 8810.1F3 (3 of 3).
- 7 Watson, J. G.; Robinson, N. F.; Chow, J. C.; Henry, R. C.; Kim, B. M.; Pace, T. G.; Meyer, E. L.; Nguyen, Q.
8 (1990a) The USEPA/DRI chemical mass balance receptor model, CMB 7.0. Environ. Software 5: 38-49.
- 9 Watson, J. G.; Robinson, N. F.; Chow, J. C.; Henry, R. C.; Kim, B.; Nguyen, Q. T.; Meyer, E. L.; Pace, T. G.
10 (1990b) Receptor model technical series, v. III (1989 revision): CMB7 user's manual. Research Triangle Park,
11 NC: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards; report no.
12 EPA-450/4-90-004. Available: <http://www.epa.gov/scram001/> [19 February 2002].
- 13 Watson, J. G.; Chow, J. C.; Lu, Z.; Gertler, A. W. (1993) Particulate and gaseous organic receptor modeling for the
14 Southern California Air Quality Study. Sacramento, CA: California Air Resource Board; report no. 8733.1F.
15 Available: <http://www.arb.ca.gov/research/apr/past/atmospheric.htm#Air%20Quality%20Study> (5 June
16 2003).
- 17 Watson, J. G.; Chow, J. C.; Lu, Z.; Fujita, E. M.; Lowenthal, D. H.; Lawson, D. R.; Ashbaugh, L. L. (1994a)
18 Chemical mass balance source apportionment of PM₁₀ during the Southern California Air Quality Study.
19 Aerosol Sci. Technol. 21: 1-36.
- 20 Watson, J. G.; Chow, J. C.; Lowenthal, D. H.; Pritchett, L. C.; Frazier, C. A.; Neuroth, G. R.; Robbins, R. (1994b)
21 Differences in the carbon composition of source profiles for diesel- and gasoline-powered vehicles. Atmos.
22 Environ. 28: 2493-2505.
- 23 Watson, J. G.; Fujita, E. M.; Chow, J. C.; Zielinska, B.; Richards, L. W.; Neff, W.; Dietrich, D. (1998) Northern
24 front range air quality study. Final report. Fort Collins, CO: Colorado State University, Cooperative Institute
25 for Research in the Atmosphere. Available: <http://www.nfraqs.colostate.edu/index2.html> (16 Jan 2002).
- 26 Watson, J. G.; Chow, J. C.; Frazier, C. A. (1999) X-ray fluorescence analysis of ambient air samples. In:
27 Landsberger, S.; Creatchman, M., eds. Elemental Analysis of Airborne Particles. Newark, NJ: Gordon and
28 Breach Science Publishers; pp. 67-96.
- 29 Weber, R. J.; McMurry, P. H.; Eisele, F. L.; Tanner, D. J. (1995) Measurement of expected nucleation precursor
30 species and 3-500-nm diameter particles at Mauna Loa Observatory, Hawaii. J. Atmos. Sci. 52: 2242-2257.
- 31 Weber, R. J.; McMurry, P. H.; Mauldin, L.; Tanner, D. J.; Eisele, F. L.; Brechtel, F. J.; Kreidenweis, S. M.; Kok, G.
32 L.; Schillawski, R. D.; Baumgardner, D. (1998) A study of new particle formation and growth involving
33 biogenic and trace gas species measured during ACE I. J. Geophys. Res. A 103: 16,385-16,396.
- 34 Weber, R. J.; Marti, J. J.; McMurry, P. H.; Mauldin, L.; Tanner, D.; Eisele, F.; Brechtel, F.; Kreidenweis, S.; Kok,
35 G.; Schillawski, R.; Baumgardner, D. (1997) Measurements of new particle formation and ultrafine particle
36 growth rates at a clean continental site. J. Geophys. Res. 102: 4375-4385.
- 37 Weber, R. J.; McMurry, P. H.; Mauldin, R. L., III; Tanner, D. J.; Eisele, F. L.; Clarke, A. D.; Kapustin, V. N. (1999)
38 New particle formation in the remote troposphere: a comparison of observations at various sites. Geophys.
39 Res. Lett. 26: 307-310.
- 40 Weber, R. J.; Orsini, D.; Daun, Y.; Lee, Y.-N.; kotz, P. J.; Brechtel, F. (2001) A particle-into-liquid collector for
41 rapid measurement of aerosol bulk chemical composition. Aerosol Sci. Technol. 35: 718-727.
- 42 Wedding, J. B.; Weigand, M. A. (1993) An automatic particle sampler with beta gauging. J. Air Waste Manage.
43 Assoc. 43: 475-479.
- 44 Weingartner, E.; Burtscher, H.; Baltensperger, U. (1997) Hygroscopic properties of carbon and diesel soot particles.
45 Atmos. Environ. 31: 2311-2327.
- 46 Weschler, C. J.; Shields, H. C. (1999) Indoor ozone/terpene reactions as a source of indoor particles. Atmos.
47 Environ. 33: 2301-2312.
- 48 Wesolowski, J. J.; John, W.; Devor, W.; Cahill, T. A.; Feeney, P. J.; Wolfe, G.; Flocchini, R. (1977) Collection
49 surfaces of cascade impactors. In: Dzubay, T. G., ed. X-ray fluorescence analysis of environmental samples.
50 Ann Arbor, MI: Ann Arbor Science Publishers, Inc.; pp. 121-131.
- 51 Whitby, K. T. (1978) The physical characteristics of sulfur aerosols. Atmos. Environ. 12: 135-159.
- 52 Whitby, K. T.; Charlson, R. E.; Wilson, W. E.; Stevens, R. K. (1974) The size of suspended particle matter in air.
53 Science (Washington, DC) 183: 1098-1099.
- 54 Whitby, K. T.; Sverdrup, G. M. (1980) California aerosols: their physical and chemical characteristics. In: Hidy,
55 G. M.; Mueller, P. K.; Grosjean, D.; Appel, B. R.; Wesolowski, J. J., eds. The character and origins of smog
56 aerosols: a digest of results from the California Aerosol Characterization Experiment (ACHEX). New York,
57 NY: John Wiley & Sons, Inc.; pp. 477-517. (Advances in environmental science and technology: v. 9).

- 1 White, W. H. (1998) Statistical considerations in the interpretation of size-resolved particulate mass data. *J. Air*
- 2 *Waste Manage. Assoc.* 48: 454-458.
- 3 Wiedensohler, A.; Hansson, H.-C.; Orsini, D.; Wendisch, M.; Wagner, F.; Bower, K. N.; Chouhrlarton, T. W.;
- 4 Wells, M.; Parkin, M.; Acker, K.; Wieprecht, W.; Facchini, M. C.; Lind, J. A.; Fuzzi, S.; Arends, B. G.;
- 5 Kulmala, M. (1997) Night-time formation and occurrence of new particles associated with orographic clouds.
- 6 *Atmos. Environ.* 31: 2545-2559.
- 7 Willeke, K.; Baron, P. A., eds. (1993) *Aerosol measurement: principles, techniques and applications*. New York,
- 8 NY: Van Nostrand Reinhold Publishers.
- 9 Willeke, K.; Whitby, K. T. (1975) Atmospheric aerosols: size distribution interpretation. *J. Air Pollut. Control Assoc.*
- 10 25: 529-534.
- 11 Williams, E. L., II; Grosjean, D. (1990) Removal of atmospheric oxidants with annular denuders. *Environ. Sci.*
- 12 *Technol.* 24: 811-814.
- 13 Williams, R.; Suggs, J.; Zweidinger, R.; Evans, G.; Creason, J.; Kwok, R.; Rodes, C.; Lawless, P.; Sheldon, L.
- 14 (2000) The 1998 Baltimore Particulate Matter Epidemiology-Exposure Study: Part 1. Comparison of ambient,
- 15 residential outdoor, indoor and apartment particulate matter monitoring. *J. Exposure Anal. Environ.*
- 16 *Epidemiol.* 10: 518-532.
- 17 Wilson, W. E. (1995) Aerosol exposure, physics, and chemistry. *Inhalation Toxicol.* 7: 769-772.
- 18 Wilson, W. E.; Suh, H. H. (1997) Fine particles and coarse particles: concentration relationships relevant to
- 19 epidemiologic studies. *J. Air Waste Manage. Assoc.* 47: 1238-1249.
- 20 Wilson, W. E.; Spiller, L. L.; Ellestad, T. G.; Lamothe, P. J.; Dzubay, T. G.; Stevens, R. K.; Macias, E. S.; Fletcher,
- 21 R. A.; Husar, J. D.; Husar, R. B.; Whitby, K. T.; Kittelson, D. B.; Cantrell, B. K. (1977) General Motors
- 22 sulfate dispersion experiment: summary of EPA measurements. *J. Air Pollut. Control Assoc.* 27: 46-51.
- 23 Woo, K.-S.; Chen, D.-R.; Pui, D. Y. H.; McMurry, P. H. (2001a) Measurement of Atlanta aerosol size distributions:
- 24 observations of ultrafine particle events. *Aerosol Sci. Technol.* 34: 75-87.
- 25 Woo, K.-S.; Chen, D.-R.; Pui, D. Y. H.; Wilson, W. E. (2001b) Use of continuous measurements of integral aerosol
- 26 parameters to estimate particle surface area. *Aerosol Sci. Technol.* 34: 57-65.
- 27 Wu, C. C.; Suarez, A. E.; Lin, Z.; Kidwell, C. B.; Borgoul, P. V.; Caffrey, P. F.; Ondov, J. M.; Sattler, B. (1998)
- 28 Application of an Ir tracer to determine soot exposure to students commuting to school on Baltimore public
- 29 buses. *Atmos. Environ.* 32: 1911-1919.
- 30 Yamasaki, H.; Kuwata, K.; Miyamoto, H. (1982) Effects of ambient temperature on aspects of airborne polycyclic
- 31 aromatic hydrocarbons. *Environ. Sci. Technol.* 16: 189-194.
- 32 Yatin, M.; Tuncel, S. G.; Tuncel, G.; Aras, N. K. (1994) Trace element composition of atmospheric aerosols in
- 33 Ankara, Turkey, determined by instrumental neutron activation analysis. *J. Radioanal. Nucl. Chem.*
- 34 181: 401-411.
- 35 Zeng, X.; Wu, X.; Yao, H.; Yang, F.; Cahill, T. A. (1993) PIXE-induced XRF with transmission geometry. *Nucl.*
- 36 *Instr. Meth. Phys. Res. B* 75: 99-104.
- 37 Zhang, X. Q.; McMurry, P. H. (1987) Theoretical analysis of evaporative losses from impactor and filter deposits.
- 38 *Atmos. Environ.* 21: 1779-1789.
- 39 Zhang, X.; McMurry, P. H. (1992) Evaporative losses of fine particulate nitrates during sampling. *Atmos. Environ.*
- 40 *Part A* 26: 3305-3312.
- 41 Zhang, X. Q.; McMurry, P. H.; Hering, S. V.; Casuccio, G. S. (1993) Mixing characteristics and water content of
- 42 submicron aerosols measured in Los Angeles and at the Grand Canyon. *Atmos. Environ. Part A*
- 43 27: 1593-1607.
- 44 Zhu, Y.; Hinds, W. C.; Kim, S.; Shen, S.; Sioutas, C. (2002a) Study of ultrafine particles near a major highway with
- 45 heavy-duty diesel traffic. *Atmos. Environ.* 36: 4323-4335.
- 46 Zhu, Y.; Hinds, W. C.; Kim, S.; Sioutas, C. (2002b) Concentration and size distribution of ultrafine particles near a
- 47 major highway. *J. Air Waste Manage. Assoc.* 52: 1032-1042.
- 48 Zoller, W. H.; Gordon, G. E. (1970) Instrumental neutron activation analysis of atmospheric pollutants utilizing
- 49 Ge(Li) γ -ray detectors. *Anal. Chem.* 42: 257-265.
- 50
- 51



APPENDIX 2A. TECHNIQUES FOR MEASUREMENT OF SEMIVOLATILE ORGANIC COMPOUNDS

Use of Denuder Systems To Measure Semivolatile Organic Compounds

Phase distribution of semivolatile organic species has been the subject of several studies that have employed denuder technology (see Gundel et al., 1995; Gundel and Lane, 1999) to directly determine the phase distributions while avoiding some of the positive and negative sampling artifacts associated with using back-up quartz filters. In an ideal system with a denuder that is 100% efficient, the gas phase would be collected in the denuder and the particle phase would be the sum of the material collected on the filter and the adsorbent downstream. Denuder collection efficiency depends on the denuder surface area (+), the diffusivity (+) and vapor pressure (-) of the compound, the temperature (-) and flow rate (-) of the air stream, and the presence of competing species (-), including water vapor (Cui et al., 1998; Kamens and Coe, 1997; Lane et al., 1988). (The + and - symbols in parentheses indicate qualitatively the effect increasing each parameter would have on efficiency). In a system with a denuder collection efficiency less than 100%, the collection efficiency must be known to accurately attribute adsorbed organics from denuder breakthrough to the gas phase and adsorbed organics volatilized from collected particles to the particle phase. In calculating the overall phase distributions of SVOC PAH from a denuder system, the collection efficiency for each compound is needed.

The efficiency of silicone-grease-coated denuders for the collection of polynuclear aromatic hydrocarbons was examined by Coutant et al. (1992), who examined the effects of uncertainties in the diffusion coefficients and in the collisional reaction efficiencies on the overall phase distributions of SVOC PAH calculated using denuder technology. In their study, they used a single stage, silicone-grease-coated aluminum annular denuder with a filter holder mounted ahead of the denuder and an XAD trap deployed downstream of the denuder. In a series of laboratory experiments, they spiked the filter with a mixture of perdeuterated PAH, swept the system with ultra-high purity air for several hours, and then analyzed the filter and the XAD. They found that the effects of these uncertainties, introduced by using a single compound as a surrogate PAH (in their case, naphthalene) for validation of the denuder collection efficiency, are less significant than normal variations because of sampling and analytical effects. Results on field studies using their sampling system have not been published.

1 For measuring particulate phase organic compounds, the denuder-based sampling system
2 represents an improvement over the filter/adsorbent collection method (Turpin et al., 1993).
3 Some researchers, however, have reported that denuder coatings themselves can introduce
4 contamination (Mukerjee et al., 1997) and that the adsorbed species may be difficult to remove
5 from the coating (Eatough et al., 1993).

6 In a study conducted in southern California (Eatough et al., 1995), the Brigham Young
7 University Organic Sampling System (BOSS; Eatough et al., 1993) was used for determining
8 POM composition, and a high-volume version (BIG BOSS; flow rate 200 L/min) was utilized
9 for determining the particulate size distribution and the chemical composition of SVOC in fine
10 particles. The BOSS, a multi-channel diffusion denuder sampling system, consists of two
11 separate samplers (each operating at 35 L/min). The first sampler consists of a multi-parallel
12 plate diffusion denuder with charcoal-impregnated filter papers as the collection surfaces
13 followed by a two-stage quartz filter pack and a two-stage charcoal-impregnated filter pack. The
14 second sampler operating in parallel with the first consists of a two-stage quartz filter pack,
15 followed by the parallel plate denuder, followed by the two-stage charcoal-impregnated filter
16 pack. The filter samples collected by the BOSS sampler were analyzed by temperature-
17 programmed volatilization analysis. The second channel allows calculations of the efficiency of
18 the denuder in removing gas-phase specifics that would be absorbed by the charcoal impregnated
19 filter. Eatough et al. (1995) also operated a two-stage quartz filter pack alongside the BOSS
20 sampler. The BIG BOSS system (Tang et al., 1994) consists of four systems (each with a
21 flowrate of 200 L/min). Particle size cuts of 2.5, 0.8, and 0.4 μm are achieved by virtual
22 impaction, and the sample subsequently flows through a denuder, then is split, with the major
23 flow (150 L/min) flowing through a quartz filter followed by an XAD-II bed. The minor flow is
24 sampled through a quartz filter backed by a charcoal-impregnated filter paper. The samples
25 derived from the major flow (quartz filters and XAD-II traps) were extracted with organic
26 solvents and analyzed by gas chromatography (GC) and GC-mass spectroscopy. The organic
27 material lost from the particles was found to represent all classes of organic compounds.

28 Eatough et al. (1996) operated the BOSS sampler for a year at the IMPROVE site at
29 Canyonlands National Park, UT, alongside the IMPROVE monitor and alongside a separate
30 sampler consisting of a two-stage quartz filter pack. They found that concentrations of
31 particulate carbon determined from the quartz filter pack sampling system were low on average

1 by 39%, and this was attributed to volatilization losses of SVOC from the quartz filters.
2 In another study conducted with the BOSS in southern California, losses of 35% of the POM, on
3 average, were found and attributed to losses of the SVOC during sampling (Eatough et al.,
4 1995).

5 The denuder used in the various BOSS samplers consists of charcoal-impregnated cellulose
6 fiber filter material. Denuder collection efficiencies of greater than 95% have been reported for
7 organic gases that adsorb on quartz and charcoal-impregnated filters (Eatough et al., 1999a; Ding
8 et al., 2002; Lewtas et al., 2001). However, because the mass concentration of gas phase species
9 that adsorb on quartz and charcoal-impregnated filters is so much greater than the mass of
10 semivolatile organic material in the particulate phase, it is necessary to measure and account for
11 the inefficiency of the denuder in the BOSS samplers. To address this problem, Brigham Young
12 University (BYU) developed a particle-concentrator (PC)-BOSS system (Ding et al., 2002;
13 Eatough et al., 1999b; Lewtas et al., 2001; Modey et al., 2001; Pang et al., 2001, 2002a,b). The
14 PC-BOSS includes a virtual impactor upstream of the denuder to improve the denuder collection
15 efficiency by removing a majority of the gases from the aerosol flow. With this system, denuder
16 collection efficiencies of greater than 99% have been reported for organic gases, $\text{SO}_2(\text{g})$,
17 $\text{HNO}_3(\text{g})$ and other species that adsorb on quartz and charcoal-impregnated filters (Pang et al.,
18 2001). Since the concentrations of semivolatile organic and other gases in the presence of the
19 concentrated particles is not altered by this process the virtual impaction concentration of
20 accumulation mode particles (except possibly by slight changes in pressure), it is anticipated that
21 the gas-particle distribution will not be significantly altered by the concentration process. The
22 virtual impactor has a 50% cut point at $0.1 \mu\text{m}$ aerodynamic diameter. As a result, some
23 particles in the 0.05 to $0.2 \mu\text{m}$ diameter size range will be removed in the major flow along with
24 the majority of the gases. Therefore, the mass collection efficiency of the virtual impactor
25 concentrator will be a function of the particle size distribution in the 0.05 to $0.1 \mu\text{m}$ size range.
26 This collection efficiency is measured by comparing the concentration of nonvolatile
27 components measured in the concentrated sample with that measured in an unconcentrated
28 sample. The concentration efficiency varies from 50 to 75%. It is relatively constant over
29 periods of weeks but varies by season and site, presumably as the particle size distribution
30 changes. Previous studies at Harvard (Sioutas et al., 1995a,b) have shown that the composition
31 of the sampled aerosol is little changed by the concentration process. The BYU studies listed

1 above have shown that the concentration efficiencies for sulfate, organic carbon (OC) and
2 elemental carbon (EC) are comparable for a given sampling location. Furthermore, the
3 concentrations of these species and of fine particulate nitrate determined using the PC-BOSS
4 have been shown to be comparable to those determined using more conventional samplers for
5 sulfate or EC or using simpler denuder systems for OC and nitrate.

6 Ding et al. (1998a) developed a method for the determination of total n-nitroso compounds
7 in air samples and used the method to examine organic compounds formed from NO_x chemistry
8 in Provo, UT (Ding et al., 1998b). In their method, n-nitroso compounds are selectively
9 decomposed to yield nitric oxide, which is then detected using chemiluminescence. From the
10 samples from Provo, they found that the majority of the n-nitroso and nitrite organic compounds
11 that were present in fine particulate matter were semivolatile organic compounds that could be
12 evaporated from the particles during sampling. They found particulate n-nitroso compound
13 concentrations ranging between <1 and 3 nmoles/m³ and gas-phase n-nitroso compound
14 concentrations in the same range. Particulate organic nitrite concentrations were found in the
15 range of <1 to ~5 nmoles/m³, and gas-phase concentrations as high as 10 nmoles/m³ were found.

16 Turpin et al. (1993) developed a sampling system that corrects for the loss of semivolatile
17 organic compounds during sampling by removal of most of the gas phase material from the
18 particles in a diffusion separator sampling system. Unlike the previously mentioned systems,
19 wherein the particulate phase is measured directly, in the system of Turpin et al. (1993) the
20 gas-phase is measured directly. In the laminar flow system, ambient, particle-laden air enters the
21 sampler as an annular flow. Clean, particle-free air is pushed through the core inlet of the
22 separator. The clean air and ambient aerosol join downstream of the core inlet section, and flow
23 parallel to each other through the diffusion zone. Because of the much higher diffusivities for
24 gases compared to particles, the SVOC in the ambient air diffuses to the clean, core flow. The
25 aerosol exits the separator in the annular flow, and the core flow exiting the separator now
26 contains a known fraction of the ambient SVOC. Downstream of the diffusion separator, the
27 core exit flow goes into a polyurethane foam (PUF) plug, where the SVOC is collected. The
28 adsorbed gas phase on the PUF plug is extracted with supercritical fluid CO₂ and analyzed by
29 gas chromatography/mass-selective detection (GC/MSD). The gas-phase SVOC is thus
30 determined. Ultimately, to determine particulate phase SVOC concentrations, the total
31 compound concentration will also be measured and the particulate phase obtained by difference.

1 The system was tested for the collection of PAH. The diffusional transport of gas-phase PAHs
2 and particle concentrations agreed well with theory. Breakthrough was problematic for low
3 molecular weight PAHs (MW < 160). Detection limits ranged from 20 to 50 pg of injected mass
4 for all PAHs.

5 Gundel et al. (1995) recently developed a technique for the direct determination of phase
6 distributions of semivolatile polycyclic aromatic hydrocarbons using annular denuder
7 technology. The method, called the integrated organic vapor/particle sampler (IOVPS), uses a
8 cyclone inlet with a 50% cutpoint of 2.5 μm at a sampling rate of 10 L/min. The airstream then
9 goes through two or three sandblasted glass annular denuders that are coated with ground
10 adsorbent resin material (XAD-4 was initially examined) that traps vapor-phase organics. The
11 airstream subsequently passes through a filter, followed by a backup denuder. The denuder
12 collection efficiency is high and compares well with predictions based on the diffusivity of the
13 compounds. The denuder can also be extracted to obtain gas-phase concentrations directly
14 (Gundel and Lane, 1999). Particle-phase PAHs are taken to be the sum of material on the filter
15 and XAD adsorbent downstream after correction for denuder collection efficiency. The IOVPS
16 was tested for sampling semivolatile PAH in laboratory indoor air and in environmental tobacco
17 smoke (ETS). After exposure, the denuders, filters, and sorbent traps were extracted with
18 cyclohexane (Gundel et al., 1995) and analyzed for PAHs from naphthalene to chrysene using
19 dual-fluorescence detection (Mahanama et al., 1994). Recoveries from both denuders and filters
20 were approximately 70% for 30 samples. Detection limits (defined as 3 times the standard
21 deviation of the blanks) for gas-phase SVOC PAHs ranged from 0.06 ng for anthracene to 19 ng
22 for 2-methylnaphthalene. The 95% confidence interval for reproduction of an internal standard
23 concentration was 6.5% of the mean value. Relative precision, from a propagation of errors
24 analysis or from the 95% confidence interval from replicate analyses of standard reference
25 material SRM 1649 (urban dust/organics), was 12% on average (8% for naphthalene to 22% for
26 fluorene). Sources of error included sampling flow rate, internal standard concentration, and
27 co-eluting peaks. Gundel and Lane (1999) reported that roughly two-thirds of particulate PAH
28 fluoranthene, pyrene, benz[a]anthracene, and chrysene were found on the postfilter denuders, so
29 that it is likely that considerable desorption from the collected particles took place.

30 Solid adsorbent-based denuder systems have been investigated by other researchers as
31 well. Bertoni et al. (1984) described the development of a charcoal-based denuder system for

1 the collection of organic vapors. Risse et al. (1996) developed a diffusion denuder system to
2 sample aromatic hydrocarbons. In their system, denuder tubes with charcoal coating and
3 charcoal paper precede a filter pack for particulate collection and an adsorption tube to capture
4 particle blow-off from the filter sample. Breakthrough curves for benzene, toluene, ortho-
5 xylene, and meta-xylene were developed for 60-, 90-, and 120-cm denuder tubes. The effects of
6 relative humidity on the adsorption capacities of the denuder system were examined, and it was
7 found that the capacity of the charcoal was not affected significantly by increases in relative
8 humidity. The feasibility of outdoor air sampling with the system was demonstrated.

9 Krieger and Hites (1992) designed a diffusion denuder system that uses capillary gas
10 chromatographic columns as the tubes for SVOC collection. The denuder was followed by a
11 filter to collect particles, which in turn was followed by a PUF plug to collect organic material
12 volatilizing off the filter. Denuder samples were analyzed by liquid solvent extraction (CH_2Cl_2)
13 followed by GC-mass spectrometric analysis. The PUF plugs and filters were extracted with
14 supercritical fluid extraction using supercritical N_2O . Using this system, an indoor air sample
15 was found to contain primarily chlorinated biphenyls, ranging from trichlorobiphenyls (vapor
16 pressures $10^{-3} - 10^{-4}$ Torr at 25°C) to octachlorobiphenyls ($10^{-6} - 10^{-7}$ Torr). This demonstrated
17 that the sampler collects compounds with a wide range of volatility. They also found that on-
18 line desorption is successful in maintaining good chromatographic peak shape and resolution.
19 The entire method, from sample collection to the end of the chromatographic separation, took
20 2 h.

21 Organic acids in both the vapor and particulate phases may be important contributors to
22 ambient acidity, as well as representing an important fraction of organic particulate matter.
23 Lawrence and Koutrakis (1996a,b) used a modified Harvard/EPA annular denuder system
24 (HEADS) to sample both gas and particulate phase organic acids in Philadelphia, PA, in the
25 summer of 1992. The HEADS sampler inlet had a $2.1\text{-}\mu\text{m}$ cutpoint impactor (at 10 L/min),
26 followed by two denuder tubes, and finally a filter pack with a Teflon filter. The first denuder
27 tube was coated with potassium hydroxide (KOH) to trap gas phase organic acids. The second
28 denuder tube was coated with citric acid to remove ammonia and thus to avoid neutralizing
29 particle phase acids collected on the filter. The KOH-coated denuder tube was reported to
30 collect gas phase formic and acetic acids at better than 98.5% efficiency and with precisions of
31 5% or better (Lawrence and Koutrakis, 1994). It was noted that for future field measurements of

1 particulate organic acids, a Na₂CO₃-coated filter should be deployed downstream of the Teflon
2 filter to trap organic acids that may evaporate from the Teflon filter during sampling.

3 4 *Role of the Collection Media*

5 The role of the collection media was recently examined in a study conducted in Seattle
6 (Lewtas et al., 2001). In that study, the influence of denuder sampling methods and filter
7 collection media on the measurement of SVOC associated with PM_{2.5} was evaluated. Activated
8 carbon and XAD collection media were used in diffusion denuders and impregnated back-up
9 filters in two different samplers, the Versatile Air Pollution Sampler (VAPS) and the PC-BOSS.
10 XAD-coated glass annular denuders and charcoal-impregnated cellulose fiber (CIF) filter
11 denuders also were used. CIF filters also were compared to XAD-coated quartz filters as backup
12 filter collection media. Lewtas et al. (2001) found that the two denuder types resulted in an
13 equivalent measurement of particulate organic carbon and particle mass. The carbon-coated
14 denuders in the BOSS sampler were more efficient than the XAD-coated denuders for the
15 collection of the more highly volatile organic compounds (MHVOC). Lewtas et al. (2001)
16 concluded that this MHVOC that is collected in the carbon-coated BOSS denuder does not
17 contribute substantially to the particle mass or to the SVOC measured as OC on quartz filters.
18 However, this MHVOC would be captured in the carbon impregnated filters placed behind the
19 quartz filters, so that, in the XAD denuder configuration, the captured MHVOC would cause a
20 higher OC concentration and an overestimation of the SVOC.

21 Some of the recent research in denuder technology also has focused on reduction in the
22 size of the denuder, optimization of the residence time in the denuder, understanding the effect
23 of diffusion denuders on the positive quartz filter artifact, identifying changes in chemical
24 composition that occur during sampling, determining the effects of changes in temperature and
25 relative humidity, and identifying possible losses by absorption in coatings.

26 27 *Reducing the Size of Denuders*

28 The typical denuder configuration is an annular diffusion denuder tube of significant length
29 (e.g., 26.5 cm for 10 L/min [Koutrakis et al., 1988a,b]). A more compact design based on a
30 honeycomb configuration was shown to significantly increase the capacity (Koutrakis et al.,
31 1993). However, in intercomparisons with an annular denuder/filter pack system (Koutrakis

et al., 1988), significant losses of ammonia and nitric acid were observed for the honeycomb configuration and were attributed to the large inlet surface area and long sample residence time of the honeycomb design relative to the annular denuder system. Sioutas et al. (1996a) subsequently designed a modified glass honeycomb denuder/filter pack sampler (HDS) with an inlet that minimizes vapor losses on the inlet surfaces. The modified HDS has reduced inlet surfaces and decreased residence time for sampled gases (NH_3 and HNO_3) compared to its predecessor (Sioutas et al., 1994d). Sioutas et al. (1996b) also tested various inlet materials (glass, PFA, and polytetrafluoroethylene [PTFE]) in laboratory tests and found that a PTFE Teflon coated inlet minimized loss of sampled gases (1 to 8% loss of HNO_3 observed, and -4 to 2% loss of NH_3 observed). The highest inlet losses were observed for HNO_3 lost to PFA surfaces (14 to 25%). The modified HDS was tested in laboratory and field tests and found to agree within 10% with the annular denuder system.

Residence Time in the Denuder

The efficiency of a diffusion denuder sampler for the removal of gas phase material can be improved by increasing the residence time of the sampled aerosol in the denuder. However, the residence time can only be increased within certain limits. Because the diffusion denuder reduces the concentration of gas-phase semivolatile organic material, semivolatile organic matter present in the particles passing through the denuder will be in a thermodynamically unstable environment and will tend to outgas SVOC during passage through the denuder. The residence time of the aerosol in the denuder, therefore, should be short enough to prevent significant loss of particulate phase SVOC to the denuder. Various studies have suggested that the residence time in the denuder should be less than about 2 s (Gundel and Lane, 1999; Kamens and Coe, 1997; Kamens et al., 1995). The residence times in the various denuder designs described by Gundel and Lane (1999) are from 1.5 to 0.2 s. The equilibria and evaporation rates are not as well understood for organic components as they are for NH_4NO_3 (Zhang and McMurry, 1987, 1992; Hering and Cass, 1999).

Effect of Diffusion Denuders on the Positive Quartz Filter Artifact

The adsorption of organic compounds by a second quartz filter has been shown to be reduced, but not eliminated, in samples collected in the Los Angeles Basin if a multi-channel

1 diffusion denuder with quartz filter material as the denuder collection surface preceded the
2 quartz filters (Fitz, 1990). This artifact can be further reduced by the use of activated charcoal as
3 the denuder surface and the use of a particle concentrator to reduce the amount of gas phase
4 organic compounds relative to condensed phase organic compounds (Cui et al., 1997, 1998;
5 Eatough, 1999). Other experiments (Cotham and Bidleman, 1992; Cui et al., 1998; Eatough
6 et al., 1995, 1996) have shown that the quartz filter artifact can result both from the collection of
7 gas phase organic compounds and from the collection of semivolatile organic compounds lost
8 from particles during sampling. Thus, results available to date suggest that both a "positive" and
9 a "negative" artifact can be present in the determination of particulate phase organic compounds
10 using two tandem quartz filters.

11 The importance of the adsorption of organic vapors on filters or PM relative to the
12 volatilization of organic compounds from PM collected on a filter continues to be a topic of
13 active debate. The relative importance of positive and negative artifacts will be different for
14 denuded and undenuded filters; will depend on face velocity, sample loading, and the vapor
15 pressures of the compounds of interest; and may vary with season and location because of
16 variations in the composition of volatile and semivolatile organic material. Evidence exists for
17 substantial positive and negative artifacts in the collection of organic PM.

19 *Changes in Chemical Composition During Sampling*

20 The use of sampling systems designed to correctly identify the atmospheric gas and
21 particulate phase distributions of collected organic material has been outlined above.
22 An additional sampling artifact that has received little consideration in the collection of
23 atmospheric samples is the potential alteration of organic compounds as a result of the sampling
24 process. These alterations appear to result from the movement of ambient air containing
25 oxidants and other reactive compounds past the collected particles. The addition of NO₂
26 (<1ppm) or O₃ (<200 ppb) to the sampled air stream (0 to 5 °C) for a high-volume sampler
27 reduced the concentrations of benzo[a]pyrene and benzo[a]anthracene from a few % to 38%,
28 with the observed reduction increasing with increased concentration of the added gases
29 (Brorström et al., 1983). Spiking a filter with an amine resulted in an increase in measured
30 concentrations of nitrosamines in both the filter and a following XAD sorbent bed for a
31 mid-volume sampler (Ding et al., 1998a,b). Similar results have been obtained for the exposure

1 of a deuterated amine on a filter to NO_x (Pellizzari and Krost, 1984). When Tenax columns
2 spiked with deuterated styrene and cyclohexene were exposed to ppm concentrations of ozone or
3 halogens, oxygenated and halogenated compounds were formed (Pellizzari and Krost, 1984).
4 Similar oxidation of aldehydes and peroxyacetylnitrate (PAN) during sampling has been
5 observed (Grosjean and Parmar, 1990). Collected PAH compounds can be oxygenated or
6 nitrated on a filter (Davis et al., 1987; Lindskog and Brorstrom-Lunden, 1987), but 1-nitropyrene
7 has been shown to be resistant to additional nitration (Grosjean, 1983). These various chemical
8 transformations of collected organic compounds can be eliminated by removal of the gas phase
9 oxidants, NO_x, HNO₃, etc., by reaction or adsorption prior to collection of the particles (Ding,
10 1998a,b; Grosjean and Parmar, 1990; Parmar and Grosjean, 1990; Pellizzari and Krost, 1984;
11 Williams and Grosjean, 1990). The BOSS denuder should be effective in eliminating most of
12 the chemical transformation artifacts because reactive gases are removed by the charcoal
13 denuder that precedes the particle collection filter.

14 15 *Temperature and Relative Humidity Effects*

16 The problems of sampling artifacts associated with SVOC adsorption and evaporation are
17 compounded by temperature and relative humidity effects (Pankow and Bidleman, 1991;
18 Pankow et al., 1993; Falconer et al., 1995; Goss and Eisenreich, 1997). Effects of temperature
19 on the partitioning of PAH were examined by Yamasaki et al. (1982), who found that the
20 partition coefficient ($PAH_{\text{vapor}}/PAH_{\text{part}}$) was inversely related to temperature and could be
21 described using the Langmuir adsorption concept. The dissociation of ammonium nitrate aerosol
22 is also a function of temperature. Bunz et al. (1996) examined the dissociation and subsequent
23 redistribution of NH₄NO₃ within a bimodal distribution using a nine-stage low-pressure Berner
24 impactor followed by analysis by ion chromatography and found a strong temperature
25 dependency on the redistribution. Bunz et al. (1996) found that at lower temperatures (below
26 10 °C) there was little change in the aerosol size distribution. At temperatures between 25 and
27 45 °C, however, the lifetime of NH₄NO₃ particles decreases by more than a factor of 10, and size
28 redistribution, as measured by average ending particle diameter, increased more for higher
29 temperatures than for lower temperatures.

30 The effects of relative humidity on the sorption of SVOC on particles are not well
31 understood. In a series of laboratory experiments, Goss and Eisenreich (1997) examined the

sorption of both nonpolar (hydrocarbons and chlorinated hydrocarbons) and polar (ethyl ether and acetone) volatile organic compounds onto combustion soot particles as a function of temperature and relative humidity. The soot particles used in their experiments were collected from oil furnaces and contained 60% (w/w) iron sulfate (water-soluble fraction) and 9% (w/w) elemental and organic carbon. They found that, for all compounds, the sorption of VOC onto soot particles decreased with increasing relative humidity over the range of 10 to 95%. They also observed hysteresis in the relative humidity dependency, with sorption coefficients at a given relative humidity higher when the RH is being increased than when the RH is being decreased. The sorption coefficients were fit with an exponential function to the RH so that the slope of the regression line would provide a measure of the influence of relative humidity. Based on the magnitude of the slope, they concluded that the RH-dependency of sorption was stronger for water-soluble organic compounds.

In another study by Jang and Kamens (1998), humidity effects on gas-particle partitioning of SVOC were examined using outdoor environmental chambers and the experimentally determined partitioning coefficients were compared to theoretical values. They examined the partitioning of SVOC onto wood soot, diesel soot, and secondary aerosols and concluded that "the humidity effect on partitioning was most significant for hydrophobic compounds adsorbing onto polar aerosols." Although these two studies seem to be contradictory, on closer examination, it is difficult to compare the two studies for several reasons. The experiments conducted by Jang and Kamens (1998) were conducted in outdoor chambers at ambient temperatures and humidities. Their model was for absorptive partitioning of SVOC on *liquid-like* atmospheric particulate matter. In contrast, the results of Goss and Eisenreich (1997) were obtained from a gas chromatographic system operated at 70 °C higher than ambient conditions. The model of Goss and Eisenreich (1997) was for adsorptive partitioning of VOC on *solid-like* atmospheric particulate matter. In the study of Jang and Kamens (1998), calculated theoretical values for water activity coefficients for diesel soot were based on an inorganic salt content of 1 to 2%; whereas, the combustion particles studied by Goss and Eisenreich (1997) contained 60% water-soluble, inorganic salt content. Jang and Kamens (1998) obtained their diesel soot from their outdoor chamber, extracted it with organic solvent (mixtures of hexane and methylene chloride), and measured the organic fraction. The resulting salt content of 2% of the

1 particulate matter studied in Jang and Kamens (1998) is enough to affect water uptake but
2 presumably not to affect the sorption partitioning of organics.

4 *Impactor Coatings*

5 Impactors are used as a means to achieve a size cutpoint and as particle collection surfaces.
6 Particles collected on impactors are exposed to smaller pressure drops than filter-collected
7 particles, making them less susceptible to volatile losses (Zhang and McMurry, 1987).
8 However, size resolution can be affected by bounce when samples are collected at low
9 humidities (Stein et al., 1994). There are other sources of error inherent in some of the currently
10 acceptable practices that could potentially affect particulate mass concentration measurements
11 and that will surely become even more important as more emphasis is placed on chemical
12 speciation. Allen et al. (1999a) reported that the practice of greasing impaction substrates may
13 introduce an artifact from the absorption of semivolatile species from the gas phase by the grease
14 because the grease could artificially increase the amount of PAHs and other organic compounds
15 attributed to the aerosol. Allen et al. (1999b) offer several criteria to ensure that this absorption
16 artifact is negligible, including selecting impaction oils in which analytes of interest are
17 negligibly soluble and ensuring that species do not have time to equilibrate between the vapor
18 and oil phases (criterion is met for nonvolatile species). They recommend using oiled impaction
19 substrates only if the absorption artifact is negligible as determined from these criteria.
20 Application of greases and impaction oils for preventing or reducing bounce when sampling with
21 impactors is not suitable for carbon analysis because the greases contain carbon (Vasilou et al.,
22 1999).

23 Kavouras and Koutrakis (2001) investigated the use of polyurethane foam (PUF) as a
24 substrate for conventional inertial impactors. The PUF impactor substrate is not rigid like the
25 traditional impactor substrate so particle bounce and reentrainment artifacts are reduced
26 significantly. Kavouras and Koutrakis (2001) found that the PUF impaction substrate resulted in
27 a much smaller 50% cut point at the same flow rate and Reynolds number. Moreover, the lower
28 50% cut point was obtained at a lower pressure drop than with the conventional substrate, which
29 could lead to a reduction of artifact vaporization of semivolatile components.

APPENDIX 2B. ANALYTICAL TECHNIQUES

2B.1 INORGANIC ELEMENTS

2B.1.1 Energy Dispersive X-Ray Fluorescence (EDXRF)

EDXRF has usually been the method of choice for analysis of trace elements on filters. EDXRF is preferred for aerosol analysis over wavelength dispersive XRF because it allows fast and simultaneous analysis over the total spectrum, allowing for the analysis of numerous elements simultaneously. EDXRF can accommodate small sample sizes and requires little sample preparation or operator time after the samples are placed into the analyzer. It also leaves the sample intact after analysis; so, further analysis is possible. XRF irradiates a uniform particle deposit on the surface of a membrane filter with 1 to 50 keV x-rays that eject inner shell electrons from the atoms of each element in the sample (Dzubay and Stevens, 1975; Jaklevic et al., 1977; Billiet et al., 1980; Potts and Webb, 1992; Piorek, 1994; Bacon et al., 1995; deBoer et al., 1995; Holynska et al., 1997; Török et al., 1998; Watson et al., 1999). When a higher energy electron drops into the vacant lower energy orbital, a fluorescent x-ray photon is released. The energy of this photon is unique to each element, and the number of photons is proportional to the concentration of the element. Concentrations are quantified by comparing photon counts for a sample with those obtained from thin-film standards of known concentration (Dane et al., 1996). The previous 1996 PM AQCD included a detailed discussion of EDXRF.

Emitted x-rays with energies less than ~4 keV (affecting the elements sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and potassium) are absorbed in the filter, in a thick particle deposit, or even by large particles in which these elements are contained. Very thick filters also scatter much of the excitation radiation or protons, thereby lowering the signal-to-noise ratio for XRF and PIXE. For this reason, thin membrane filters with deposits in the range of 10 to 50 $\mu\text{g}/\text{cm}^2$ provide the best accuracy and precision for XRF and PIXE analysis (Davis et al., 1977; Haupt et al., 1995).

2B.1.2 Synchrotron Induced X-ray Fluorescence (S-XRF)

S-XRF is a form of EDXRF in which the exciting x-rays are derived from a synchrotron. Bremsstrahlung x-rays are generated when energetic electrons (generally several GeV in

energy) are forced by a magnetic field to make a bend in their path. The advantages of the technique are that an extremely high flux of x-rays may be obtained and that the x-rays are 100% polarized in the plane of the electron beam. The former allows for x-ray beams generally of 50 to 500 μm in diameter. However, the beams can be focused into x-ray microprobes, with spot sizes on the order of one μm diameter. The x-ray polarization allows for removal of most of the background normally found under the characteristic x-ray peaks, greatly improving sensitivity compared to other XRF techniques. The primary disadvantages are the limited number of synchrotrons, and that few synchrotrons have S-XRF capabilities. Thus, the technique has been relatively little used for PM, and then generally for special problems such as the smoke from the Kuwaiti oil fires (Cahill et al., 1992, Reid et al., 1994). However, with the increasing availability of S-XRF facilities dedicated to PM analysis, the first of which was the Advanced Light Source opened at Lawrence Berkeley National Laboratory last year, utilization of S-XRF for PM analysis is increasing.

2B.1.3 Proton (or Particle) Induced X-ray Emission (PIXE)

PIXE differs from XRF analysis in the excitation source for producing fluorescence. The filter deposit is bombarded with high-energy protons to remove inner shell electrons and the resulting characteristic x-rays are analyzed as in XRF (Johansson, 1970, Cahill, 1981, 1985; Zeng et al., 1993). Small accelerators, generally Van de Graaffs, generate intense beams of low energy protons, generally of a few MeV in energy. These have the ability to remove electrons from inner shells of atoms of any element. Thus, PIXE can see a very wide range of elements in a single analysis. The cross section for producing x-rays using protons of a few MeV in energy tends to favor lighter elements, Na through Ca, but sensitivities for equivalent PIXE and multi-wavelength XRF analysis are roughly comparable. The technique has been widely used in the U.S. (Flocchini et al., 1976, Malm et al., 1994) and around the world, as many universities have the small accelerators needed for the method. Like S-XRF, the proton beams can be focused into μm size beams, but these have been relatively little used for PM. However, the mm size beams used in both S-XRF and PIXE are well suited to analyzing the limited mass and small deposits that result from detailed particle size measurements by impactors (Perry et al., 1999).

2B.1.4 Proton Elastic Scattering Analysis (PESA)

With the routine availability of elemental analyses for all elements sodium and heavier, organic components remain the major unmeasured species for mass balance. For programs like IMPROVE (Malm et al., 1994), parallel filters are collected for separate organic and elemental carbon determinations. Aerosol programs that use PIXE can directly measure hydrogen simultaneously by scattering protons from Teflon filters that lack hydrogen (Cahill et al., 1989, 1992). Generally, results from organic matter by carbon combustion from quartz filters and organic matter by hydrogen from Teflon filters are in agreement, assuming certain assumptions about the chemical states of sulfates and nitrates are met (Malm et al., 1994, Cahill et al., 1996).

2B.1.5 Total Reflection X-ray Fluorescence (TRXRF)

One of the limitations of the EDXRF method is the minimum detection limit, which may be high due to high background values (Streit et al., 2000). By implementation of x-ray optical geometries that use the total reflection of the primary radiation on flat surfaces, scattering on the substrate is reduced, so that detection limits can be reduced. This is the basis for the total reflection x-ray fluorescence (TRXRF) method (Aiginger and Strelt, 1997). This modification to the EDXRF technique improves detection limits and avoids the need to correct for matrix effects. Despite its apparent advantages, TRXRF has not yet become widely in use for atmospheric aerosol analysis but has been used in the analysis of marine aerosol (Stahlschmidt et al., 1997) and at a high elevation site (Streit et al., 2000). Streit et al. sampled ambient air at the High Alpine Research Station (3580 m above sealevel) in the Bernese Alps, Switzerland, using a nine-stage, single-jet, low-pressure, cascade impactor equipped with quartz impactor plates coated with silicon oil diluted in 2-propanol. The typical sample volume for a weekly sample was 10 m³. The quartz plates were analyzed directly by TRXRF. Streit et al. reported that the minimum detection limits, defined by the 3 σ values of the blanks, ranged from 25 ng for S, decreased monotonically with increasing atomic number down to 5 pg for Rb, and decreased after that. The use of TRXRF is expected to increase as EDXRF users become aware of the method. A relatively low-cost, add-on unit has been developed that would allow EDXRF users to test the TRXRF technique (Aiginger, 1991).

2B.1.6 Instrumental Neutron Activation Analysis (INAA)

INAA irradiates a sample in the core of a nuclear reactor for few minutes to several hours, depending on the elements being quantified (Dams et al., 1970; Zoller and Gordon, 1970; Nadkarni, 1975; Landsberger, 1988; Olmez, 1989; Ondov and Divita, 1993). The neutron bombardment chemically transforms many elements into radioactive isotopes. The energies of the gamma rays emitted by these isotopes identify them and, therefore, their parent elements. The intensity of these gamma rays is proportional to the amount of the parent element present in the sample. Different irradiation times and cooling periods are used before counting with a germanium detector. In source apportionment studies, it is possible to use a combination of XRF and INAA to develop a relatively complete set of elemental measurements. Between these two analytical techniques, good sensitivity is possible for many elements, including most of the toxic metals of interest. In general, XRF provides better sensitivity for some metals (e.g., Ni, Pb, Cu, and Fe); whereas INAA provides better sensitivity for others (Sb, As, Cr, Co, Se, and Cd). Both methods provide similar detection limits for still other elements (V, Zn, and Mn). INAA does not quantify some of the abundant species in ambient particulate matter such as silicon, nickel, tin, and lead. While INAA is technically nondestructive, sample preparation involves folding the sample tightly and sealing it in plastic, and the irradiation process makes the filter membrane brittle and radioactive. These factors limit the use of the sample for subsequent analyses.

INAA has been used to examine the chemical composition of atmospheric aerosols in several studies either as the only method of analysis or in addition to XRF (e.g., Yatin et al., 1994; Gallorini, 1995). INAA has higher sensitivity for many trace species, and it is particularly useful in analyzing for many trace metals. Landsberger and Wu (1993) analyzed air samples collected near Lake Ontario for Sb, As, Cd, In, I, Mo, Si, and V using INAA. They demonstrated that using INAA in conjunction with epithermal neutrons and Compton suppression produces very precise values with relatively low detection limits.

Enriched rare-earth isotopes have been analyzed via INAA and used to trace sources of particulate matter from a coal-fired power plant (Ondov et al., 1992), from various sources in the San Joaquin Valley (Ondov, 1996), from intentionally tagged (iridium) diesel emissions from sanitation trucks (Suarez et al., 1996; Wu et al., 1998), and from iridium-tagged emissions from school buses (Wu et al., 1998).

1 An intercomparison was conducted in which 18 pairs of filters were sent to participants in
2 the Coordinated Research Program (CRP) on Applied Research on Waste Using Nuclear Related
3 Analytical Techniques (Landsberger et al., 1997). As part of that study, participants used PIXE,
4 INAA, XRF, or AAS to analyze the samples. Many of the results for XRF and PIXE in the
5 coarse fraction were observed to be biased low compared to INAA. The authors speculated that
6 there is a systematic error because of self-attenuation of the x-rays resulting from the particle
7 size effect.

9 **2B.1.7 Atomic Absorption Spectrophotometry (AAS)**

10 AAS is applied to the residue of a filter extracted in a strong solvent to dissolve the solid
11 material; the filter or a portion of it is also dissolved during this process (Ranweiler and Moyers,
12 1974; Fernandez, 1989; Jackson and Mahmood, 1994; Chow et al., 2000a). A few milliliters of
13 this extract are injected into a flame where the elements are vaporized. Elements absorb light at
14 certain wavelengths in the visible spectrum, and a light beam with wavelengths specific to the
15 elements being measured is directed through the flame to be detected by a monochrometer. The
16 light absorbed by the flame containing the extract is compared with the absorption from known
17 standards to quantify the elemental concentrations. AAS requires an individual analysis for each
18 element, and a large filter or several filters are needed to obtain concentrations for a large variety
19 of elements. AAS is a useful complement to other methods, such as XRF and PIXE, for species
20 such as beryllium, sodium, and magnesium which are not well-quantified by these methods.
21 Airborne particles are chemically complex and do not dissolve easily into complete solution,
22 regardless of the strength of the solvent. There is always a possibility that insoluble residues are
23 left behind and that soluble species may co-precipitate on them or on container walls.

24 AAS was used to characterize the atmospheric deposition of trace elements Zn, Ni, Cr, Cd,
25 Pb, and Hg to the Rouge River watershed by particulate deposition (Pirrone and Keeler, 1996).
26 The modeled deposition rates were compared to annual emissions of trace elements that were
27 estimated from the emissions inventory for coal and oil combustion utilities, iron and steel
28 manufacturing, metal production, cement manufacturing, and solid waste and sewage sludge
29 incinerators. They found generally good agreement between the trend observed in atmospheric
30 inputs to the river (dry + wet deposition) and annual emissions of trace elements, with R^2 's
31 varying from ≈ 0.84 to 0.98. Both atmospheric inputs and emissions were found to have

1 followed downward trends for Pb. For the period of 1987 to 1992, steady increases were
2 observed for Cd (major sources are municipal solid waste incineration, coal combustion, sludge
3 incineration, and iron and steel manufacturing), Cr and Ni (major sources are iron and steel
4 production and coal combustion), and Hg (major sources are coal, the contribution from which
5 had decreased from 53 to 45%, and municipal, solid, and medical waste incineration, the
6 contribution from which has increased).

7 8 **2B.1.8 Inductively Coupled Plasma with Atomic Emission Spectroscopy** 9 **(ICP-AES)**

10 ICP-AES introduces an extracted sample into an atmosphere of argon gas seeded with free
11 electrons induced by high voltage from a surrounding Tesla coil (Fassel and Kniseley, 1974;
12 McQuaker et al., 1979; Lynch et al., 1980; Harman, 1989; Tyler, 1992; Baldwin et al., 1994).
13 The high temperatures in the induced plasma raise valence electrons above their normally stable
14 states. When these electrons return to their stable states, a photon of light is emitted that is
15 unique to the element that was excited. This light is detected at specified wavelengths to identify
16 the elements in the sample. ICP-AES acquires a large number of elemental concentrations using
17 small sample volumes with acceptable detection limits for atmospheric samples. As with AAS,
18 this method requires complete extraction and destruction of the sample.

19 20 **2B.1.9 Inductively Coupled Plasma with Mass Spectroscopy (ICP-MS)**

21 ICP-MS has been applied in the analysis of personal exposure samples (Tan and Horlick,
22 1986; Gray and Williams, 1987a,b; Nam et al., 1993; Munksgaard and Parry, 1998; Campbell
23 and Humayun, 1999). Ion species generated from ICP and from the sample matrix can produce a
24 significant background at certain masses resulting in formation of polyatomic ions that can limit
25 the ability of ICP-MS to determine some elements of interest. Cool plasma techniques have
26 demonstrated the potential to detect elements at the ultra-trace level (Nham et al., 1996) and to
27 minimize common molecular ion interferences (Sakata and Kawabata, 1994; Turner, 1994;
28 Plantz, 1996). Detection limits of ICP-MS using a one-second scan are typically in the range of
29 10^{-3} ng/m³, which is an order of magnitude lower than other elemental analysis methods. The
30 instrument can also be set up to analyze a wide dynamic range of aerosol concentrations.